Catalysis by Metal Complexes 39

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Arno Behr
Andreas J. Vorholt

Homogeneous Catalysis with Renewables

Springer

Catalysis by Metal Complexes

Volume 39

Catalysis by Metal Complexes

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Series Editors

Prof. D.J. Cole-Hamilton
EaStChem, School of Chemistry
University of St Andrews
Purdie Building, North Haugh
St Andrews, Fife KY16 9ST
Scotland, UK

Prof. Piet W.N.M. van Leeuwen
Institute of Chemical Research of Catalonia
Av. Paisos Catalans 16
43007 Tarragona
Spain

Volume 39
Homogeneous Catalysis with Renewables

Volume Authors

Arno Behr
Department of Biochemical and Chemical Engineering
Technische Universität Dortmund
Dortmund
Germany

Andreas J. Vorholt
Department of Biochemical and Chemical Engineering
Technische Universität Dortmund
Dortmund
Germany

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Arno Behr
Department of Biochemical and Chemical Engineering
Technische Universität Dortmund
Dortmund
Germany

Andreas J. Vorholt
Department of Biochemical and Chemical Engineering
Technische Universität Dortmund
Dortmund
Germany

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Chapter 1
Introduction

Arno Behr and Andreas J. Vorholt

1.1 Advantages of Homogeneous Catalysis in Derivatisation of Renewables

In “green chemistry”, catalysis is a very helpful tool to convert basic chemicals into valuable fine and specialty products. By decreasing the energy of activation, the catalysts enable reactions which are not possible to carry out without the catalyst. This general rule is valid both for classical petrochemicals and of course for renewables. Depending on the molecular structure of the renewables (see Sect. 1.2), the reaction types may differ but the basis ideas remain the same.

Catalysis can be divided into different sections depending either on mechanistic considerations or on the methods of application. Very useful is the distinction between heterogeneous and homogeneous catalysis, but also special areas as biocatalysis, organocatalysis, photocatalysis or electrocatalysis can be considered. In the present book, the homogeneous catalysis takes centre, especially the homogeneous catalysis with transition metal complexes. Homogeneous catalysts are always solved in a liquid which may be a fluid starting compound or a solvent.

The transition metals have—compared to the main group metals—a number of important advantages in catalysis: They have free d-orbitals or even f-orbitals, through which they are able to interact with many reactants and with numerous ligands. Thus, an “inactive” ethene or carbon monoxide molecule can bind on the catalyst metal and can react as an activated intermediate with further compounds. Transition metals can also easily change their coordination number and ligand field. Thus, the catalytic complexes can be “tailored” for the specific reaction with the desired molecule. Too, transition metals occur in different oxidation states which can be changed easily. Thus, oxidative addition reactions or reductive eliminations are readily done. All these advantages of organometallic chemistry can be applied in homogeneous transition metal catalysis.

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The row of valuable catalyst metals starts from the left side of the periodic table to the right: group 3 and group 4 metals are very useful for homogenous catalysed polymerisations, group 5 till 7 metals are often applied in oxidations or metathesis reactions, and the group 8 metals, especially the noble metals rhodium, palladium, iridium and platinum, are applied extensively e.g. in hydrogenations or carbonylations. Many of these catalytic complexes are easily synthesised by reproducible protocols, and their stoichiometry and structure are well known and readily analysable. As analytic methods in homogeneous catalysis, often spectroscopic techniques are used. Because all reactants and products, but also the starting catalyst and the catalytic intermediates are solved in a liquid phase, the classical organic analysis methods such as NMR, IR or UV-VIS can be adopted thus giving a deep insight into the mechanistic pathway of the reaction. If the mechanism is well known, the chemist can further optimise the reaction, often via adjustment of the reaction conditions, the reactor type or the composition of the catalytic complex e.g. via ligand tailoring.

The high variability of the complex ligand field is one of the big advantages of homogeneous transition metal catalysis. The number of ligands is overwhelming: monodentate ligands, carbenes, hemilabile ligands, chelates or higher multidentate ligands can be used; ligands with phosphorus, nitrogen, oxygen or other elements as binding atoms can be applied. Ligands with different electronic and steric properties can steer the reaction into the right direction.

This “steering effect” of the ligand field is the “plus point” of homogeneous catalysis: reactions can be carried out with very high selectivities, such as chemo-, regio-, stereo- or even enantioselectivities. Enantioselective reactions are of high importance in fine and specialty chemistry, e.g. for pharmaceuticals or agrochemicals. Enantioselective ligands date from the “chiral pool” of nature or can be synthesised in the laboratory. Chiral catalysis enables the directed synthesis only of the active components without formation of unwanted by-products, thus preserving our resources and avoiding harmful waste.

A further advantage of homogenous transition metal catalysis is the fact that this kind of catalysis often operates under very smooth conditions. Metal complexes are usually not stable at higher temperatures; thus, the catalytic reactions must occur at low temperatures e.g. in the range of room temperature till 150 °C. Also the pressures used in homogeneous catalysis are generally low, e.g. in the range of 1–40 bar. Thus—in comparison with many heterogeneous catalysed reactions—energy can be saved, and the apparatus can be constructed at relatively low costs. Renewables such as sugars or unsaturated fats are often sensitive against high temperature and pressures. Thus, homogeneous catalysis is a useful tool to convert them without unwanted breaking of bonds.

In chemical industry besides of activity and selectivity of the transition metal catalysts also the stability and lifetime of the catalyst is of high importance. In classical laboratory optimisations, this point is often insufficiently considered. To the comprehensive development of a catalyst, also the stability has to be tested in detail, for instance in continuously operated miniplants (see Chaps. 8–11) in which the homogeneous catalyst is monitored for a longer reaction period e.g. for several days or even weeks. Catalyst recycling is absolutely required to make the catalytic reaction economically feasible, especially if noble metals or valuable ligands are used. Only the results of such detailed investigations allow the decision of the industrial use of a new catalyst.

Catalysis and renewables are the two important pillars of “green chemistry”. By using this combination, atom economic reactions can be carried out without significant by-products. Because of high selective reactions waste can be prevented. Homogeneous catalysis also enables the minimising of the energetic requirements of a chemical process: some reactions can even be conducted at ambient temperature and pressure. Thus, the catalytic reactions of renewables may lead to an enlarged number of valuable chemical products without damage of the environment and at acceptable costs.

In this book, important homogenously catalysed reactions and their application in continuously operated miniplants are highlighted. Hydrogenation, hydroformylation, aminations, telomerisations and oxidations were chosen as platforming reactions, in which homogeneous catalysis plays a role. Metatheses were recently reviewed; therefore, these reactions are subsumed in the chapter tandem reactions. Here, combinations of reactions can transform renewables in one preparative step into valuables. The rarely reported developments of homogenous catalysed reactions into continuously operated miniplants are differentiated also by reaction type, telomerisation, codimerisation, hydroamination and hydroformylation.

1.2 Introduction into the Chemistry of Renewables

Renewables are defined as natural compounds which grow again every year. They are produced in agriculture and forestry and are applied (predominantly) in the non-food area. These applications can be in chemistry or in producing energy. Especially, organic waste materials are of special interest for the use in industry, for instance saw mill waste or straw. Also, material of marine origin e.g. seaweed belongs to the big group of renewables. Instead of “renewables”, the term “biomass” is generally used, and the non-food biomass is called, too, “industrial biomass”. Besides herbal, animal feedstocks can also be utilised for instance tallows from slaughterhouses which can be processed to soaps.

The source of all these renewables is finally the light of the sun: by **photosynthesis,** carbon dioxide and water react to carbohydrates and oxygen as shown in Eq. 1.1:

$$nCO_2 + nH_2O \Rightarrow (CH_2O)_n + nO_2 \tag{1.1}$$

In biology, one distinguishes between primary and secondary substances. **Primary substances** are materials which are essential for the growth and the reproduction of the plants. They are responsible for the stability and elasticity of the plants or serve as energy buffer. For instance, sugar beets store their energy supply as sucrose in their roots. Important primary substances of plants are carbohydrates, lignin, fats and oils and proteins:

- The most common **carbohydrates** in nature are the macromolecular compounds cellulose, chitin, starch and hemicelluloses and the low-molecular carbohydrates mono- and disaccharides. Cellulose and hemicelluloses occur in wood and natural fibres, chitin in the shell of crabs and cancers, starch in many crop plants such as potatoes, corn, wheat and peas and mono- and disaccharides such as glucose, fructose or sucrose in numerous fruits, in beet roots and in sugar cane.
- **Lignin**—a macromolecular compound with aliphatic and aromatic structures—is a main component of wood.
- **Fats and oils** are triglycerides which appear in crops such as soy bean, rapeseed, sunflower or coconuts.
- **Proteins** are polyamides formed by amino acids. They are also found in numerous crops e.g. in soy beans.

The most important **secondary substances** occur only in small amounts in nature; however, they are important for the plant to repel aggressors or to attract dusting insects. Prominent examples are as follows:

- **Terpenoids** such as mono- or polyterpenes which occur in pins or rubber trees.
- Natural **colourants** such as alizarin or indigo.
- Natural **scents** such as essential oils of rose, jasmine or violets.
- Natural **drugs** such as pyrethroids, alkaloids or steroids.
- **Vitamins** such as the water-soluble vitamin C or the oil-soluble vitamin E.

It was estimated that 170 billion tons of renewables are formed by nature every year. The highest percentage of this huge amount forms the cellulose with about 39%, and all other carbohydrates sum up to 26%. The next 30% is given by lignin; the remaining 5% are all other renewables including the group of fats and oils. Till now, manhood is using only 6 billion tons of this biomass annually that means about 3.5 weight-percentage.

At the present time, chemical industry is using predominantly crude oil and natural gas as feedstocks for the production of organic chemicals; however, these fossil feedstocks are confined and must be replaced gradually by renewables. Currently, the chemical industry is already using renewables in a certain amount: in Germany, 17 Mio t of petrochemicals were produced in 2006, compared to 2.7 Mio t of products on the basis of renewables. Therefore, the fraction of renewables is at about 14 weight-percentage which is a little bit higher in Germany than in most other countries. Interestingly, the main part of renewables used in industry is herbal or animal fats and oils. The reason for this high share is the fact that fats and oils are chemically relatively simple molecules which resemble in their structure to the well-known petrochemical basic chemicals: the hydrocarbon chains of fatty compounds enable similar chemical conversions as with petrochemicals, and especially, catalytic conversions can be easily accomplished with fats and oils.

However, although the share of biomass is increasing in the last decades, the use of renewables in industry has also some **limitations**: one important problem can be the **acquisition** of the renewable feedstocks. Whereas crude oil and natural gas can be excavated in a relatively efficient manner on particular places, the renewables must be collected with high effort in a widespread agricultural or forest area. The same problem occurs if natural waste material must be collected, for instance saw dust from numerous saw mills or straw from a great number of harvested grain fields. Acquisition of renewables means often expansive and time-consuming transport arrangements. This fact influences substantially the economics of a chemical process using renewables.

Another problem is connected with the molecular structure and elemental composition of certain renewables. The big group of carbohydrates contains large amounts of oxygen e.g. in terms of aldehyde or hydroxyl groups which make the compounds very hydrophilic i.e. water soluble. Whereas common petrochemistry works preferentially with water-insoluble hydrocarbons, the handling of carbohydrates requires totally other reaction concepts. One alternative is to “defunctionalise” the carbohydrates by dehydration or hydrogenative dehydration yielding compounds similar to the well-known petrochemical hydrocarbons. Here, the fats and oils as well as the terpenoids have great advantages because they have similar structures to petrochemicals.

1.3 Introduction into the Main Groups of Renewables

1.3.1 Oleochemicals

Fats and oils are triglycerides i.e. esters of long-chain carboxylic acids with glycerol (1,2,3-propane triol). These carboxylic acids are called “fatty acids”. By hydrolysis of triglycerides with water, the so-called fat splitting or fat hydrolysis, the fatty acids can be set free. In triglycerides, the three fatty acids can be identical, but also different. In nature, almost exclusively even fatty acids occur; their chain length is usually in the range of C12 till C22. They can be not only saturated such as palmitic acid (C16) or stearic acid (C18), but also unsaturated. Important unsaturated fatty acids (Fig. 1.1) are as follows:

- Oleic acid (C18) with one *Z* double bond in C9-position
- Linoleic acid (C18) with two *Z* double bonds in the C9- and C12-positions
- Linolenic acid (C18) with three *Z* double bonds in the C9-, C12- and C15-positions
- Erucic acid (C22) with one *Z* double bond in C13-position.

These double bonds are of great importance of the reactivity of the molecules, because unsaturated fatty acids or esters cannot only react on the carboxyl group but can catalytically be converted, too, to interesting follow-up products via addition on

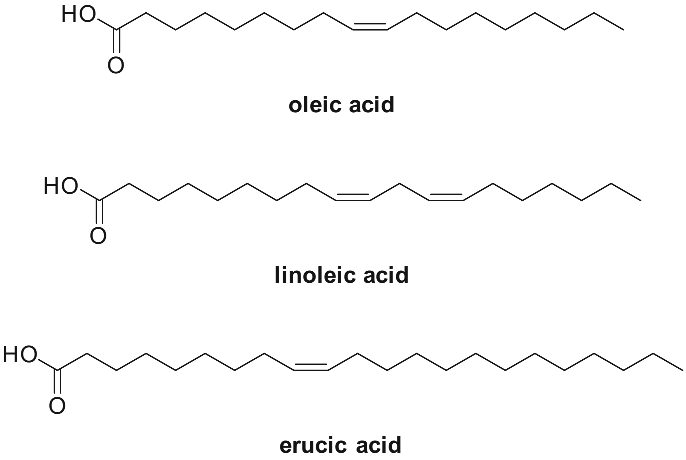


Fig. 1.1 Important unsaturated fatty acids

their CC-double bonds. Also, saturated fatty compounds can be functionalised on the alkyl chain, however, usually not selectively via radical substitution reactions.

The most important **fats and oils** (by mass of production) are palm oil, soy bean oil, rape seed oil and sunflower oil. Besides these four big fat resources, palm kernel oil, coconut oil and animal fats such as tallow and grease are also of importance for use in chemical industry.

- **Palm oil** and **palm kernel oil** arise in the same source, the fruits of the oil palm. The numerous fruits contain a soft pulp which contains triglycerides with predominantly saturated and unsaturated C16- and C18 fatty acids. The kernel of the oil palm fruit, however, contains a fat with a high amount of triglycerides with short-chain carboxylic acids such as lauric acid (C12) and myristic acid (C14). Oil palms have origin in the rain forests of Guinea, but today they grew predominantly in plantations of Indonesia and Malaysia.
- The **coconut palm** provides the coconut oil, which contains triglycerides which resemble very much the palm kernel oil. Once again, the short-chain fatty acids (C12–14) predominate (65%); the remaining acids are C16- and C18 acids. Similar to oil palms, coconut palms also grew in the equatorial zone.
- **Rape seed oil** is an important oil which stems from the temperate zones. The classical rape seed contains a great amount (50%) of erucic acid which is not convenient as human food. By breeding, a new type of rape seed oil was developed, the 00-type of rapeseed oil. It contains high amounts of oleic acid and linoleic acid and can therefore be used as food.
- **Soy bean oil** stems from soy beans which contain high amounts of proteins (40%) and a lower amount of oil (20%). This oil is obtained by extraction and contains 50% of linoleic acid, 30% of oleic acid and 3–11% of linolenic acid. It also contains lecithins which can be used as emulsifiers both in food preparation

and in technical applications. The residue of the extraction contains the proteins and the carbohydrates and is used as food in soy milk, in soy flour and in tofu. For technical applications, the high content of linoleic acid is of importance: varnishes and paints, lubricants and plasticizers are made on the basis of soy oil. In recent years, polyols stemming from soy oil are used as starting compounds for bio-polyesters and bio-polyurethanes.

- **Sunflower oil** derives from sunflowers which originally occurred in Northern America but came to Europe in the sixteenth century. The flower contains thousands of sunflower seeds whose content of oil amounts to 57%. The "old" sunflower oil contains predominantly linoleic acid (44–70%) and oleic acid (14–43%) and can be used for soaps and varnishes. By breeding, the "new" high oleic type was established yielding oleic acid in high yield (91%) and purity. Thus, this type is very suitable for the production of detergents, paints and cosmetics.
- Important **animal fats** are tallow, grease and fish oils. The grease is a collective name for spreadable fats stemming from pigs and geese. Tallow is a fat predominantly from cows or wethers. Grease and tallow contain especially oleic, palmitic and stearic acids. Fish oils are only produced in small amounts for food applications and contain useful polyunsaturated fatty acids, the so-called PUFAs.

1.3.2 Terpenes

Terpenes are very well known since hundreds of years, especially because of their widespread applications as flavours and fragrances. They are extracted from trees, fruits and flowers via different methods. According to Wallach's rule, terpenes are composed of isoprene, i.e. branched C5-units. Hence, a distinction is drawn between monoterpenes (C10), sesquiterpenes (C15), diterpenes (C20) and triterpenes (C30). Also, longer terpenes are known, for instance the polyterpene natural rubber, which is a *cis*-poly(isoprene), and the gutta-percha, which is the isomeric *trans*-poly(isoprene). The structure of the terpenes can be very variable: there are a great number of acyclic hydrocarbons, but also mono-, bi- to pentacyclic derivatives exist. The reason why they are interesting for homogeneous catalysis is the fact that most of them are unsaturated and contain CC-double bonds which can coordinate to metal complexes. Acyclic monoterpenes like myrcene contain three double bonds, monocyclic monoterpenes like limonene contain two double bonds, and bicyclic monoterpenes such as α-pinene, β-pinene, 3-carene or camphene contain only one double bond (Fig. 1.2).

However, not only saturated terpenes exist in nature, such as pinane, but also functionalised terpenes occur such as terpene alcohols (such as nerol, geraniol, citronellol and menthol), terpene aldehydes (such as citronellal and citral) or terpene ketones (such as carvone or camphor) (Fig. 1.3).

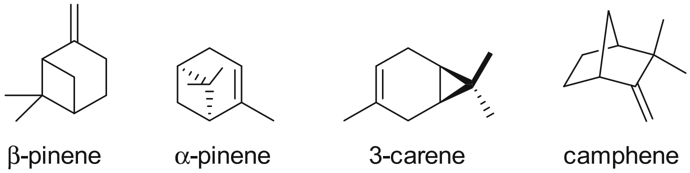


Fig. 1.2 Acyclic and cyclic monoterpene hydrocarbons

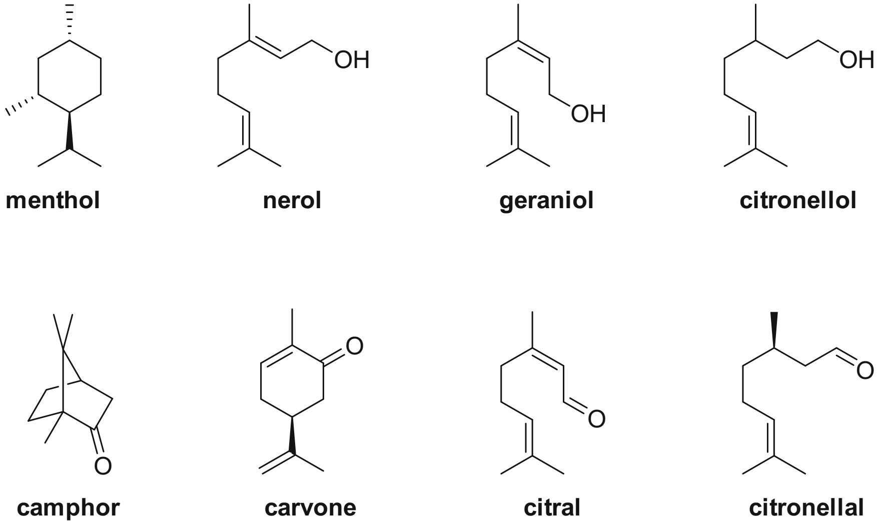


Fig. 1.3 Functionalised monoterpenes

Important higher terpenes are e.g. the sesquiterpenes bisabolene and farnesene as well as the diterpene retinol (Fig. 1.4):

- **Bisabolenes** (with different positions of the double bonds) are present in the essential oils of lemon and oregano. They function also as pheromones of different insects.
- **α-Farnesenes** occur in apple skins and cause the typical odour of green apples. The isomeric **β-farnesenes** can be found in different essential oils. Certain potato species use it as natural insect repellent.
- **Retinol** is an essential fat soluble vitamin (Vitamin A_1) and occurs in numerous animal and plant food.

Respective to the quantity, the most important source of terpenes is turpentine which is a broad mixture of volatile terpene compounds stemming from the tree resin of conifers. Depending on the starting material and the production method, the turpentine is classified into three categories:

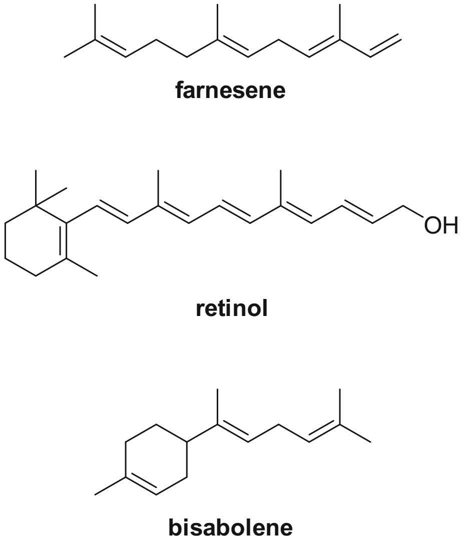


Fig. 1.4 Examples for sesqui- and diterpenes

- **Wood turpentine** is obtained via steam distillation or extraction with hydrocarbons or chlorohydrocarbons of old chopped wood stumps. This process is based on the fact that the resin level is particularly high in the lower trunk section. However, because of the dwindling supply of tree stumps, this route has become less important.
- **Gum turpentine** derives from the balsam of living trees. An incision is made into the trunks to collect the crude balsam in bottles or bags. For example, black pines afford annually up to 5 kg balsam. The further processing takes place via vacuum distillation, where colophony remains as residue. Because of its high purity gum, turpentine is very suitable for further syntheses. The main producer worldwide is the PR China; the biggest producer in Europe is Portugal.
- **Sulphate turpentine** is a cheap by-product in pulp production via the sulphate process (“Kraft process”). In this process, wood chips of cut trees are partially solubilised in NaOH by addition of Na_2S, Na_2SO_4 and Na_2SO_3. The crude sulphate turpentine is obtained from the condensate of the waste gas. However, also after further purification and oxidation steps, sulphate turpentine still contains some contaminations with sulphur compounds. The biggest producer worldwide is the USA; great producers in Europe are Scandinavia and Russia.

The most abundant ingredients of turpentine are the two pinenes (see Fig. 1.2) which serve as starting compounds for the synthesis of flavours, fragrances and pharmaceuticals. A major part is used for the industrial manufacture of camphor which is applied as plasticizer in celluloid production. A certain amount is used for the synthesis of myrcene via pinene pyrolysis at a temperature of 450–500 °C. This isomerisation occurs with a very short retention time (5 s) followed by a quick quenching step. The maximum myrcene yield amounts to 85%. Myrcene has both isolated and conjugated double bonds and is therefore an interesting model compound for homogeneous catalysed reactions.

A great number of terpenes are isolated from fruits, flowers and herbs, e.g. from citrus fruits, coriander, roses, cloves, violets, salvia and rosemary. The essential oils are obtained via steam distillation, extraction and “enfleurage” which is an absorption of the volatile terpenes in a layer of fat. To get very pure individual terpenes, a careful fractionated distillation has to be performed. Some important examples of the production of functionalised monoterpenes are as follows:

- **Nerol** is isolated from lavender and essences of roses
- **Geraniol** and **citronellol** are extracted especially from geranium
- **Citronellal** stems from lemons and limes
- **Citral** is the main component of lemon grass
- **Menthol** occurs in mint and peppermint plants.

1.3.3 Carbohydrates

The name “carbohydrates” originally stems from the expression “hydrates of carbon”, which was used because of the elementary composition $C_nH_{2n}O$. In a formal way, this formula can also written as $C_n(H_2O)_n$, thus explaining this (wrong) denomination. Today, often the name “saccharides” is chosen and one differentiates between:

- Monosaccharides (such as glucose and fructose)
- Disaccharides (such as sucrose and lactose)
- Further oligosaccharides (like the trisaccharide raffinose) and
- Polysaccharides (such as cellulose and starch).

The low-molecular saccharides, the sugars, are water soluble and have a sweet flavour, whereas the polysaccharides are water insoluble and tasteless. By definition, the saccharides contain one aldehyde or one keto group and at least two hydroxy groups. A typical example for a hydroxyaldehyde is D-glucose; an example for a hydroxyketone is D-fructose (see Fig. 1.5).

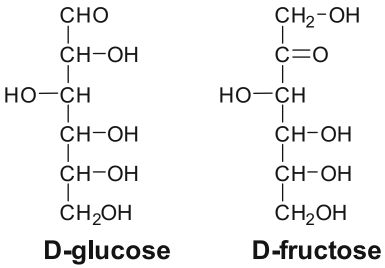


Fig. 1.5 Linear formulas of D-glucose and D-fructose

Saccharides which contain an aldehyde group are called aldoses; saccharides with keto groups are ketoses. The monosaccharides contain three to six carbon atoms and have the names trioses (3 C), tetroses (4 C), pentoses (5 C) and hexoses (6 C). Using this nomenclature, the glucose belongs to the group of aldohexoses and fructose to the group of ketohexoses. Both exist in two enantiomeric isomers: in nature exists only the D-glucose, whereas the non-natural L-glucose is only available synthetically and is of no importance. Also, fructose exists in D- and L-enantiomers.

D-Glucose ($C_6H_{12}O_6$), also named "grape sugar" or "dextrose", is the main product of photosynthesis and is stored in nature in polymers as starch (in plants) or as glycogen (in animals). It is already frequently used in chemical industry especially in fermentations. Starting from D-glucose, both ethanol and amino acids, citric acid and lactic acids are accessible by fermentation reactions. Also, metal catalysed conversions of D-glucose are carried out e.g. the hydrogenation of D-glucose to the sugar alcohol D-sorbitol which is both a low-caloric sweetening agent and an important starting compound for the synthesis of vitamin C.

The ketohexose **D-fructose** is also called "fruit sugar", because it is found in many tree fruits, vine fruits, melons, beets and berries. D-Fructose has a very sweet taste (about 1.7 times sweeter than sucrose). In industry, starch is disintegrated enzymatically to D-glucose which is than isomerised (also enzymatically) to a mixture of D-fructose (45%) and D-glucose (55%). This "high-fructose corn syrup" (HFCS) is often used as sweetener in foods and drinks. A non-food application of fructose is the dehydration to 5-(hydroxymethyl) furfural, which is widely discussed as platform compound in chemical industry.

Both aldohexoses and ketohexoses exist not only in a linear structure (see Fig. 1.5), but also in cyclic structures. This is shown in the following on the example of D-glucose: the aldehyde function can react with the hydroxy group on position 5, thus yielding a hemiacetal (Fig. 1.6). By this reaction, a new hydroxy

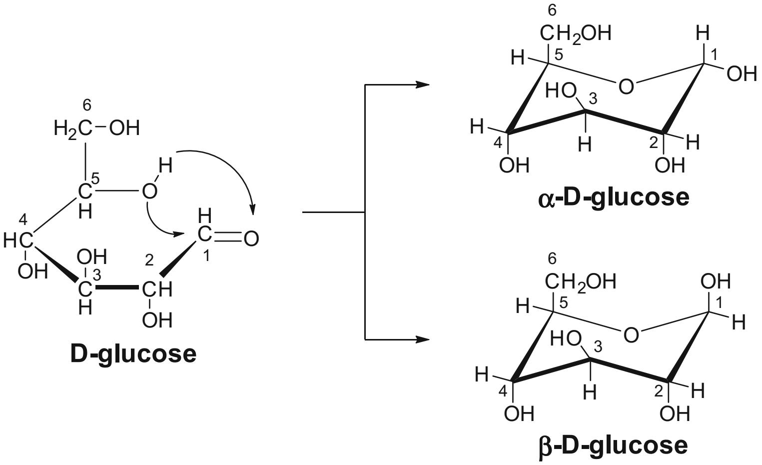


Fig. 1.6 The anomers α-D-glucose and β-D-glucose

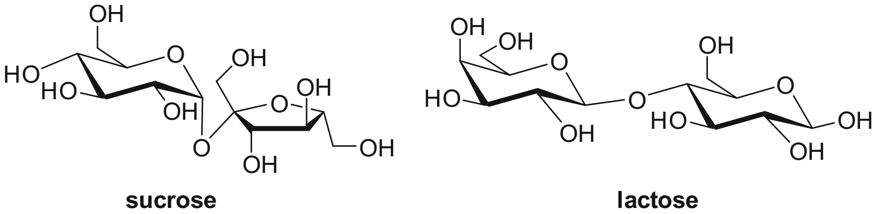


Fig. 1.7 Formula of the disaccharides sucrose and lactose

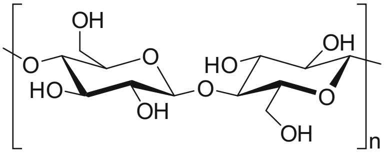
group is formed on carbon atom 1 which can be oriented in α- or in β-position. Thus, we have to differentiate between the isomers α-D-glucose and β-D-glucose which are called “anomers”.

The most important disaccharide is **sucrose** which is simply named “sugar” in everyday life. It is produced from sugar cane and sugar beet in an amount of about 180 million tons per year (2014/15). In sucrose, the α-D-glucose is linked with β-fructose as shown in Fig. 1.7. Many industrial applications of sucrose are based on fermentation reactions. The splitting of the sucrose molecule into its monosaccharides succeeds by using the glucoside hydrolase enzyme “invertase” yielding the “invert sugar syrup”. Sucrose can also be converted into sucralose, a zero-calorie artificial sweetener, or into isomaltose, a tooth-friendly sucrose replacement especially for diabetics.

The disaccharide **lactose** can be found in milk and dairy products. The molecule consists of the two monosaccharides β-galactose and β-glucose which are bound through a β-1,4-glycosidic linkage (see also Fig. 1.7). Lactose is applied in infant nutrition and as matrix material in the pharmaceutical industry. Also, a number of chemical conversions of lactose are well known, e.g. hydrogenations, oxidations and isomerisations.

Cellulose consists of some hundreds up to 10,000 monomeric β-D-glucose units which are linked together in a β-1,4 manner (Fig. 1.8). This polysaccharide is unbranched, and therefor, the cellulose chains can easily have contact to each other via hydrogen bridging bonds. The key resource of cellulose is wood in which the cellulose occurs together with hemicelluloses and lignin (see Sect. 1.3.4). More than 2 billion tons of wood are lumbered every year whereof a great part is used as timber or firewood. Only 13% of the wood is processed further, e.g. by the “Kraft process” in which the cellulose is separated from hemicelluloses and lignin by a mixture of sodium sulphide and sodium hydroxide. The resulting cellulose or

Fig. 1.8 Molecular structure of cellulose



"pulp" is predominantly used for the production of paper and cardboards, and only 4% are used for chemical conversions.

Important secondary products of cellulose are as follows:

- Cellulose esters (such as cellulose acetate or cellulose nitrate)
- Cellulose ethers (such as carboxymethyl cellulose or ethyl cellulose)
- Regenerated cellulose which is applied to make fibres (e.g. rayon) or films (e.g. cellophane).

Starch is—like cellulose—also composed of monomeric β-D-glucose units; however, the linkage is done in an α-1,4-manner. The linear polymer formed is called amylose. Depending on the source of the starch, also branched polymer chains occur. By additional α-1,6-glycosidic linkages, the amylopectin molecules are formed (Fig. 1.9).

Starch can be isolated from different plants e.g. from corn, wheat, rice, barley, potatoes or manioc. It is used frequently in the paper, thickener and binder industry. It can be applied not only in the production of biodegradable thermoplastic materials, but also in the pharmaceutical, cosmetic or food sector. By enzymes or acids, starch can be hydrolysed selectively to oligomers or to the monomer D-glucose. By oxidation, complexing agents can be synthesised which are used in the detergent industry. Just as cellulose, starch can also be converted into starch esters (e.g. acetates or phosphates) or ethers (e.g. carboxymethyl starch or hydroxyethyl starch).

1.3.4 *Lignin*

Lignin is a major component of wood. Depending on the type of wood, it contains 20–30% lignin, 40–55% cellulose and 30–35% hemicelluloses. Thus, wood is a

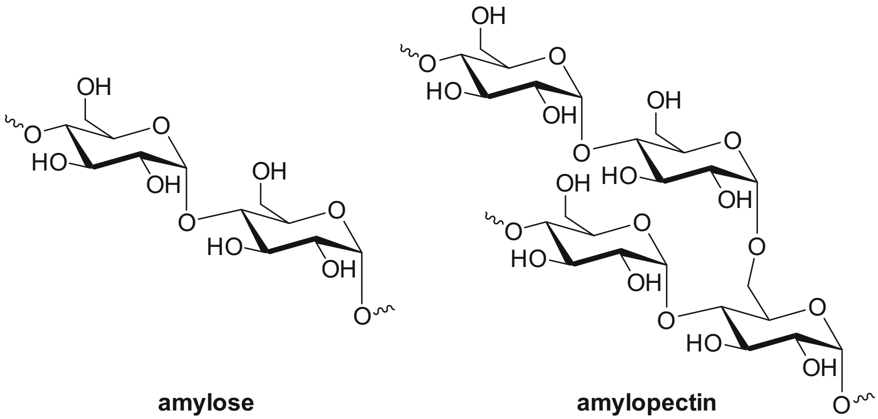


Fig. 1.9 Molecular structures of amylose and amylopectin

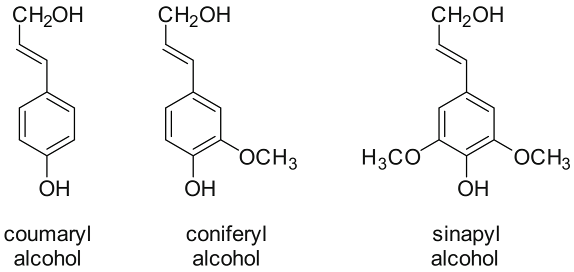


Fig. 1.10 Monomeric lignin constituents

composite material in which the lignin is basically responsible for the stability. Lignin is a macromolecule which is formed from aromatic monomers, especially coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Fig. 1.10).

Lignin is water insoluble, and only partially soluble in acids, bases or special solvents like pyridine. In the manufacture of cellulose (see Sect. 1.3.3), lignin is a side product which is produced in amounts of more than 55 million tons per year. However, it is usually not isolated, but burnt to provide the thermal energy for the paper mills. The types of linkage in the macromolecule lignin are very diverse, and it is a big challenge to open selectively these linkages, thus yielding valuable aromatic compounds e.g. phenol or substituted phenols. There are some decomposition methods which use not only acids (e.g. nitric, acetic or formic acid) or bases (e.g. sodium hydroxide, ammonia or ethanol amine), but also solvents such as ethanol or methanol or special activators like anthrachinone. Also, hydrogenation of lignin or enzymatic methods are under investigation. So far, the use of lignin is comparatively limited: one application is the production of vanillin via oxidative treatment with strong bases or the formation of duromeric resins. Because of the dispersing and emulsion-stabilising properties of lignin, it is also used in cement applications, water treatment or oilfield applications.

1.3.5 Peptides

In peptides, α-amino acids are linked together forming amides. Two amino acids form a dipeptide; molecules with a greater number of amino acids are called oligopeptides. If the molecular weight is in the range of about 6000 to about 1 million, these substances are polypeptides or proteins (Fig. 1.11). In nature, all proteins are formed from 22 natural occurring α-amino acids. The simplest α-amino

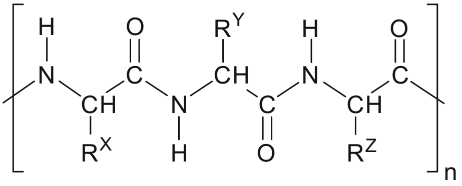


Fig. 1.11 General molecular structure of proteins

acid is the amino acetic acid glycine. In all other α-amino acids, the α-C-atom is an asymmetrically substituted carbon atom, thus yielding chiral molecules. Natural proteins are formed by L-amino acids e.g. by leucine, valine, tyrosine or methionine.

The sequence of the L-amino acids gives the primary structure of the protein. However, by the formation of hydrogen bridges, secondary structures are formed like the α-helix structure or the β-pleated sheet structure. Additional bonds can be formed like disulphide bridges between two cysteine units.

Proteins can be synthesised from the amino acids via stepwise condensation reactions with the elimination of water. In nature, this composition of the protein structure is regulated by the desoxyribonucleic acids of the genes. Vice versa, the proteins can be hydrolysed into the amino acids both by strong acids and by specific enzymes.

All animal or plant cells contain proteins. Typical animal protein sources are meat, fish, eggs, milk, cheese and yoghurt; plant protein sources are e.g. soy beans, beans, manioc, lentils or chick peas.

1.3.6 Carbon Dioxide

In a certain way, also carbon dioxide is a “renewable”. It is consistently formed by nature in the biospheric cycle: The plants die off and are reconverted to CO_2 and water via microorganisms. In addition, mankind uses fossil raw materials such as oil, gas and coal especially for energy production, thus producing great amounts of anthropogenic carbon dioxide. In the last 150 years, the emissions of CO_2 have increased in a nearly exponential manner, and mankind is trying to stop and reduce these emissions as good as possible. One (small) possibility is to use carbon dioxide as a C1 source for chemical applications. The anthropogenic emission of CO_2 is estimated to 30 billion tons per year; the range of use of carbon dioxide in chemical industry is (today) only estimated to 0.2 billion tons per year.

The problem is that carbon dioxide is a very stable molecule: this colourless and inodorous gas is extremely inert and resists also high temperatures. It presents the highest oxidation state of carbon and is difficult to reduce or to functionalise. But there are some possibilities to activate CO_2:

- The reduction with hydrogen gas e.g. to formic acid or its stable derivatives
- The reaction with molecules which have high energy-containing groups such as epoxides, dienes or alkines
- The reaction to products which are very stable, e.g. salts

There are already some applications of carbon dioxide in chemical industry, in parts for many years (Fig. 1.12):

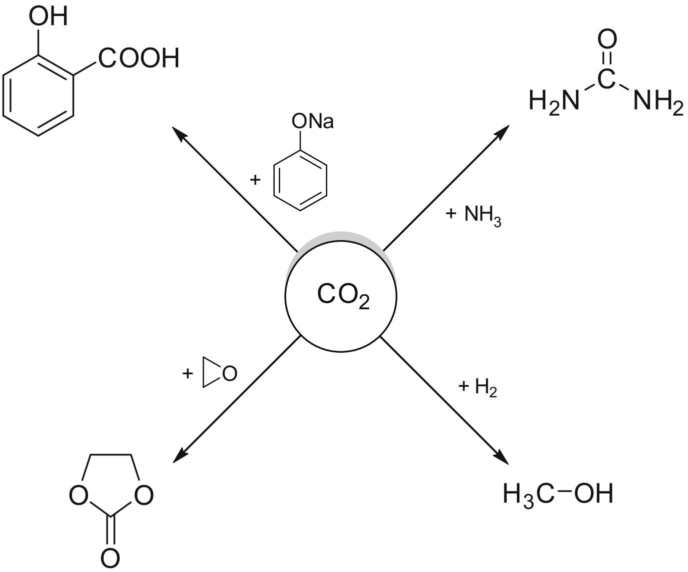


Fig. 1.12 Today' applications of carbon dioxide

- The synthesis of urea from carbon dioxide and ammonia (more than 100 Mio t/a)
- The supplement of CO_2 to synthesis gas which is used for methanol production (2 Mio t/a)
- The reaction of CO_2 with epoxides to cyclic carbonates or to polycarbonates (50.000 t/a)
- The conversion with sodium phenolate to salicylic acid (25.000 t/a).

However, one important tool to activate carbon dioxide is not yet fully investigated: the activation by transition metal catalysis. By coordination to metal complexes, the linear and stable CO_2 molecule is influenced by the electron field of the metal and is bound e.g. in nonlinear way which enables the reaction with other molecules. There are a number of interesting catalytic applications under investigation (Fig. 1.13):

- The nickel catalysed conversion of ethene with CO_2 to acrylic acid
- The palladium catalysed telomerisation of 1,3-butadiene with CO_2 yielding lactones
- The nickel or rhodium catalysed reaction of CO_2 with alkines to pyrones
- The ruthenium catalysed hydroformylation of alkenes with CO_2/H_2 mixtures to aldehydes
- The ruthenium catalysed hydrogenation of CO_2 to formic acid
- The iron or cobalt catalysed co-polymerisation of CO_2 with epoxides.

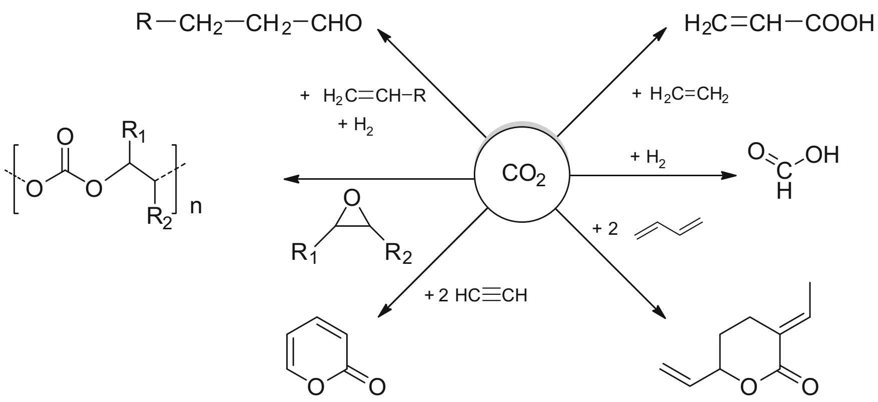


Fig. 1.13 Carbon dioxide applications under investigation

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Chapter 2
Hydrogenation of Renewables

Andreas J. Vorholt and Arno Behr

2.1 Introduction

Hydrogenation reactions have a variety of applications in the chemical industry which is shown by the corresponding products, such as ammonia, methanol, and polyamides. In petrochemistry, the addition of hydrogen is used to adjust properties of product mixtures, e.g. in the hydrocracking or hydrotreating. For renewables the same is already feasible or first proofs of concept were already shown. Therefore, hydrogenations indicate ways to increase the availability and enhance handling of products from natural resources. Heterogeneously catalysed hydrogenations with renewables are realised already in big scale, e.g. in the production of margarine or sorbitol.

In general, hydrogenation is the addition of hydrogen to C–C-, C–O-, C–N-, or N–O-multiple bonds. If the bond is broken, the reaction is referred to as hydrogenolysis [1]. Hydrogenation reactions are usually exothermic; therefore, low temperatures favour the reaction over its corresponding back reaction, which is dehydrogenation (Fig. 2.1).

Hydrogenations on industrial scale are mostly heterogeneously catalysed but lack of reactivity at mild reaction conditions or selectivity. Therefore, homogeneous catalysed hydrogenations are needed for more specialised reactions, which are required for the valorisation of renewables.

Common catalyst metals for homogeneous hydrogenations are platinum, palladium, rhodium, iridium, and ruthenium. But also non-precious metal systems as nickel, copper and other transition metals, such as molybdenum and cobalt have found applications in industrial processes. Frequently used homogeneous catalyst complexes in hydrogenation are as follows:

$$A + n\,\mathrm{H}_2 \rightleftharpoons B \quad \Delta H_r < 0$$

Fig. 2.1 General reaction equation of hydrogenation

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Catalysis by Metal Complexes 39, DOI 10.1007/978-3-319-54161-7_2

- Wilkinson-type catalysts like $RhCl(PPh_3)_3$ and the corresponding ruthenium or iridium species
- Hydride species like $Rh(CO)_2(PPh_3)H$
- Chelate complexes with chiral ligands like the Binaphos (see Fig. 2.4)
- Ru-Carbene complexes
- Special pincer ligands have high activity in the hydrogenation of, for example, CO_2.

The present chapter is structured by the substrates of hydrogenation. In the first part, CO_2 as an inactive resource with carbon in a high oxidative state and with a low energy content as substrate is described. In this respect, homogeneous catalysts are able to gain valuable chemicals from this side product of burning or fermentation processes, e.g. methanol or formic acid.

The second part describes processing renewables, such as fatty acids and lignin via hydrogenation. These highly complex mixtures that contain various molecules and are oxygen rich compared to petrochemicals are defunctionalised or depolymerised via hydrogenation in order to gain more uniform blends.

2.2 Hydrogenations of Carbon Dioxide

Back in the 1980s, there were just a few research groups who dealt with the conversion of the “inactive” CO_2 [2–7]. The flashlight on carbon dioxide utilisation was set during the climate discussion and the impact of carbon dioxide to the greenhouse effect. Numerous efforts were put in the development of catalysts to process CO_2 as a chemical feedstock [8–11]. Beside this development, also photochemical and electrochemical reactions are in the statu nascendi with various materials from metal complexes, organic compounds, and transition metal electrodes [12–29]. The homogenously catalysed reduction of carbon dioxide focuses on formic acid and methanol as products. These C_1- molecules can act as hydrogen storage, as these molecules are liquid at ambient conditions. While formic acid contains 4.4 wt% of hydrogen, methanol contains 12.6 wt%. The stored hydrogen preferably originates from the electrolysis of water using solar energy from where a lot of effort is invested lately [27, 30–35]. The synthesis of formic acid [36] formate salts [37, 38] or methanol [39, 40] is entropically disfavoured, wherefore different bases are applied in the formation of formic acid (Fig. 2.2). If water is used as solvent, the carbonate/bicarbonate equilibrium also plays a role in the hydrogenations. Calculations showed that hydrogenation of the bicarbonate to formates is exergonic [41].

The formation of formic acid (FA) and formate amine salts was numerously studied in the last years. Also systems of hydrogenation and dehydrogenation with one catalyst system were developed. The following Table 2.1 gives an overview on several catalyst systems.

$$CO_2(g) + H_2(g) \rightleftharpoons HCO_2H(l)$$

$$\Delta G^0 = 32.8\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta H^0 = -31.5\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta S^0 = -216\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

$$CO_2(g) + H_2(g) + NH_3(aq) \rightleftharpoons HCO_2^-\ (aq) + NH_4^+(aq)$$

$$\Delta G^0 = -9.5\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta H^0 = -84.3\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta S^0 = -250\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

$$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(l) + H_2O(l)$$

$$\Delta G^0 = -9.5\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta H^0 = -131\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta S^0 = -409\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

Fig. 2.2 Gibbs energy of the hydrogenation of CO_2

First attempts to hydrogenate CO_2 were already made by Inoue in 1976 by applying triphenylphosphine with Ru-, Ir-, and Rh-complexes in benzene. The solvents applied in this hydrogenation of CO_2 play a crucial role for stabilising intermediate catalytic species. The Wilkinson complex has higher reaction rates in more polar solvents like methanol [43]. Also supercritical CO_2 itself as solvent in its state is possible, wherein also hydrogen is highly soluble [47]. The group of Jessop reported a TOF up to 95.000 h^{-1} with $RuCl_2(OAc)(PMe_3)_4$ as catalyst precursor with different amines and alcohols [48]. The role of these additives is still object of investigation, but it is reported that the formate generation needs a Lewis base, while the alcohol additive is proton donor.

The role of water in the solvent mixtures was investigated since faster reactions were reported if water was present [56]. Reactions in water were first shown in the

Table 2.1 Catalyst systems for the formation of formic acid and its salts from $CO_{2,}$ for abbreviations see Figs. 2.4 and 2.5

Catalyst precursor	Solvent	Additive	*P* (H_2/CO) MPa	*T*/°C	Rct. time/h	TON	TOF/h^{-1}	References
		Phosphine ligand						
$RuH_2(PPh_3)_4$	C_6H_6	Et_3N/H_2O	2.5/2.5	rt	20	87	4	[42]
$RhCl(PPh_3)_3$	DMSO	Et_3N	2/4	25	20	2.500	125	[43]
$[Rh(cod)Cl]_2$/dppb	DMSO	Et_3N	2/2	rt	22	1.150	30–47	[44]
$RhCl(tppts)_3$	H_2O	$NHMe_2$	2/2	rt	12	3.440	290	[45, 46]
$l_2(PMe_3)_4$	$scCO_2$	Et_3N	8.5/12	50		7.200	1.040	[47]
$RuCl(OAc)\ (PMe_3)_4$	$scCO_2$	Et_3N/C_6F_5OH	7/12	50	0.33	32.000	95.000	[48]
$[RuCl_2(tppms)_2]_2$	H_2O	$NaHCO_3$	6/3.5	80	0.03		9.600	[49]
$Fe(BF_4)_2/PP_3$	MeOH	$NaHCO_3$	6/0	80	20	610	30	[50]
IrH_3(P1)	H_2O/THF	KOH	4/4	120	48	3.500.000	73.000	[51, 52]
RuH(Cl)(CO)(P3)	DMF	DBU	2/2	70	2	38.600		[53]
RuH(Cl)(CO)(P3)	DMF	DBU	3/1	120			11.00000	[54]
		Nitrogen ligand						
$[Cp^*Ir(DHPT)Cl]^+$	H_2O	KOH	3/3	120	48	222.000	(33.000)	[55]

early 1990 by Leitner with rhodium and sulfonated phosphine ligands (see Fig. 2.4), [57], and this concept was transferred to other ligands and metals [45, 49, 58–61]. TOFs of up to 9.600 h^{-1} were found with $[RuCl_2TPPMS_2]_2$. Besides, the sulfonated ligands also water-soluble amine-based ligands were used [62–65]. Beller and Laurenczy showed that if $[RuCl_2(C_6H_6)]_2$ is used also simple phosphine ligands such as TPP can form an active catalyst system in an aqueous $NaHCO_3$ solution. The ligand diphenylphosphinomethane DPPM showed TOFs of up to 1.260 h^{-1} but is fast deactivated. However, also phosphite ligands are reported [66].

The combination of ionic liquids (IL) and sulfonated ruthenium phosphine complexes was used to form a continuous operated process to gain pure formic acid under supercritical conditions (Fig. 2.3).

The optimisation of the process parameters was performed in a batch mode, especially the identification of the suitable IL. The 1-ethyl-3-methylimidazolium chloride (EMIMCl) was selected while the anion HCO_2^- showed the highest activity under continuous conditions. The extraction of the formic acid was the limiting factor of this system [67].

The group of Hicks established another concept of catalyst recycle by the immobilisation of Ir-complexes on mesoporous silica tethered surfaces. These concepts give a TON of 2800 after 20 h [68]. Laurenczy proved with the $[RuCl_2(PTA)_4]$ (see Fig. 2.4) the stability of the complex by producing FA without base under mild conditions. This system was recycled four times showing a constant activity [69].

Another step to a commercial hydrogenation of carbon dioxide is the use of non-precious metals as catalyst metal due to their lower cost. These opportunities were investigated by Beller with Co-precursors and PP_3 (see Fig. 2.4) as ligand which yield a TON of over 3.500 [70]. If very strong bases like the Verkade base are applied with 2 MPa CO_2/H_2, a TOF of 74.000 h^{-1} was achieved [71]. Also Fe complexes show activity in the hydrogenation with TONs of up to 7.500 [72].

Pincer ligands (see Fig. 2.5) are another highly promising aspect of hydrogenation of CO_2 since Nozaki reported on the trihydride iridium species with the PNP-pincer ligand (2,6-bis(diisopropylphosphinomethyl)pyridine) which showed the highest reported TOF (150.000 h^{-1}) and TON (3.5 mio after 48 h) at a temperature of 200 °C and 8 MPa in THF/water [51, 52]. In the following, also, other air-stable pincer ligands with lower activities were reported [73] and pincer ligands

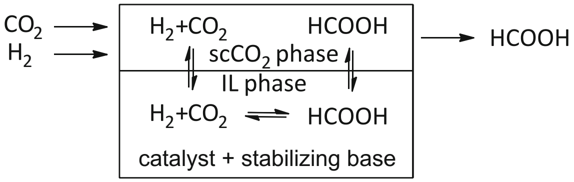


Fig. 2.3 Continuous-flow hydrogenation of CO_2 to formic acid based on a biphasic reaction system

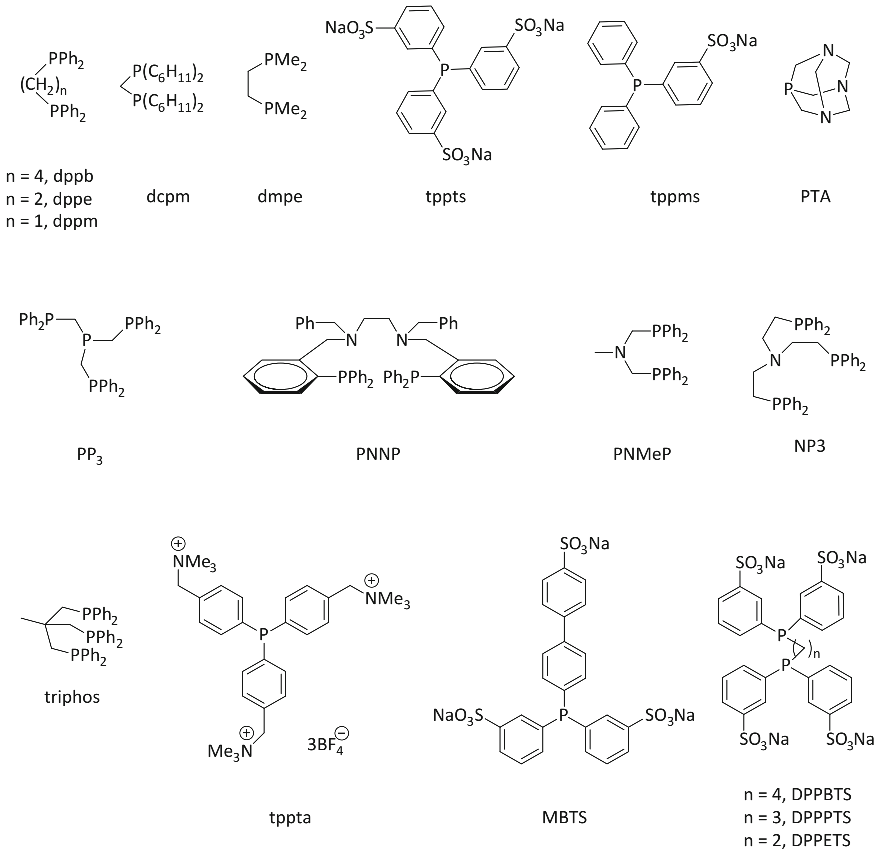


Fig. 2.4 Active phosphine ligands in the hydrogenation of CO_2

which use Fe as a catalyst metal [74]. Pidko reported on a Ru-based pincer catalyst which increases the TOF to 1.100.000 h^{-1} in a DMF/DBU system [54].

Like in other filed of homogeneous catalysis, N-heterocyclic carbenes were applied also in this field. The electron-donating ligands [75] showed with iridium TONs of up to 190.000 at 200 °C and 6 MPa in 75 h [76, 77].

Only a few examples of N,N- or N,C-Ligands were reported so far [78–80]. These complexes are highly pH sensitive in respect of activity and solubility. The iridium-4DHBP catalyst complex [Cp*Ir-(4DHBP)Cl]Cl can be attributed to TOF of 42,000 h^{-1} and TON of 190,000 at 120 °C and 6 MPa. Noteworthy is activity of the catalyst at ambient temperature and pressure with the TOF of 7 h^{-1}. The pH switch can also be used as a trigger to precipitate such catalyst complexes in order to recycle them [81, 82]. While $[Cp^*Ir(4DHBP)(OH_2)]^{2+}$ is still soluble in the water phase (1 ppm) even at optimised pH conditions, $[Cp^*Ir(DHPT)(Cl)]^{+}$ has a very low solubility in the product mixture of acidic FA/formate solution in a pH range of 4–7 (lowest concentration at pH 5 with 100 ppb). The filtration of the catalyst had

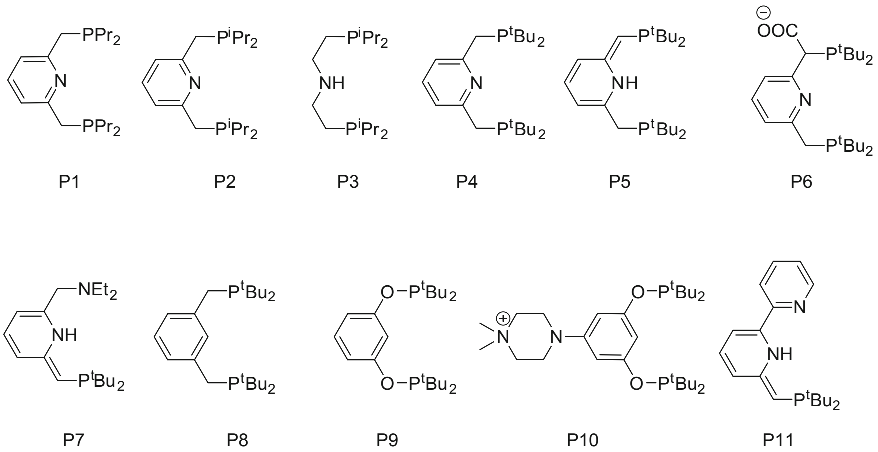


Fig. 2.5 Hydrogenation active pincer ligands

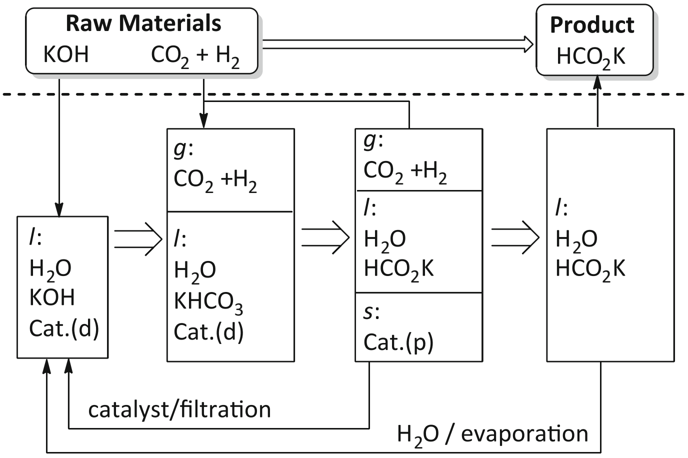
an efficiency of 91% after three runs, and the activity was retained over these recycling runs [55].

2.2.1 Interconversion of CO_2/Formic Acid as Hydrogen Storage

In order to use the hydrogenation of CO_2 as liquid hydrogen storage not only the reaction to formic acid (FA) is important, but also the dehydrogenation of FA plays an important role [83, 84]. The concept of interconversion with one catalyst system was first realised by Leitner who used a Rh/DPPB catalyst system in a FA/NEt_3/acetone mixture in order to gain a hydrogenation TOF of 54 h^{-1} and a dehydrogenation TOF of 40 h^{-1} [85]. The very effective NPN Pincer iridium catalyst system for the hydrogenation is not active in the dehydrogenation [52]. If other additives like triethanolamine or NaOH are used, TOFs of up to 1.000 h^{-1} were observed for the dehydrogenation (Fig. 2.6).

The systems can be switched from hydrogenation to dehydrogenation by temperature and pressure [86, 87] or pH value [88]. Olah and co-workers presented a temperature controlled reversible hydrogen storage system in which a Ru pincer complex catalysed the hydrogenation of CO_2 in a water/THF system at 70–85 °C and 4–8 MPa. The dehydrogenation is executed at 69 °C with the same catalyst complex. The recovery of the formed FA was completed after 4.5 h with 90% yield and could be repeated for six times with a total TON of 11.500.

The pH-controlled system is using the circumstance that at high pH values the hydrogenation is favoured while at low pH the dehydrogenation is faster (Fig. 2.7). This behaviour was shown with the $[(Cp^*IrCl)_2(THBPM)]^{2+}$ complex which is



g: gas phase, *l:* liquid phase, *s:* solid phase,
cat.(d): deprotonated form, cat.(p): protonated form.

Fig. 2.6 Recycling system for the conversion of CO_2/H_2 into HCO_2K using $[Cp^*Ir(DHPT)(Cl)]^+$ in aqueous KOH solution

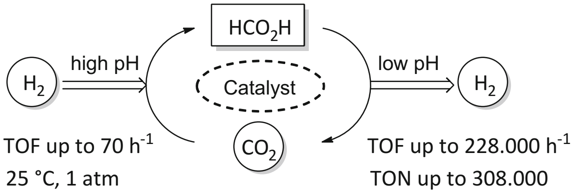


Fig. 2.7 pH-controlled hydrogen storage

active at ambient conditions with a TOF of 70 h^{-1} towards the FA and a TOF for the dehydrogenation of 228.000 h^{-1} at 90 °C and low pH value. This cycle was repeated twice by adding acid or base to the system, respectively.

2.2.2 Methanol

The hydrogenation of formic acid, urea, or CO_2 can also be used to yield methanol in a more sustainable fashion in comparison with the route via syngas, which is gained from the partial oxidation of naphtha or steam reforming of methane. The

$$3HCO_2H(aq) \rightarrow CH_3OH(aq) + H_2O(aq) + 2CO_2(g)$$

$$\Delta G^0_{298} = -23.5\ \text{kcal mol}^{-1}$$

Fig. 2.8 Disproportionation of formic acid to methanol

examples to use homogeneous catalysis in this case are rare, but these examples are qualified by high efficiency.

For urea derivatives, organic carbonates, carbamates, and formates as products from carbon dioxide, Milstein showed that a PNN-Ru(II) pincer complexes [Ru(P7)(H)-(CO)] and [Ru(P11)(H)(CO)] produce methanol under mild conditions [89]. The high TON of 4.400 for the substrate dimethyl carbonate at 5 MPa, H_2 at 110 °C, is a promising example on the indirect hydrogenation [89].

The use of the above-described FA route in combination with the followed disproportionation of FA yields methanol [90] (Fig. 2.8). After the first investigation with iridium catalysts [90], Cantat reported a significantly improved precursor [Ru(cod)(methylallyl)$_2$], with triphos ($CH_3C(CH_2PPh_2)_3$) as ligand and MSA (methanesulfonic acid) as catalytic system [91].

The direct hydrogenation of CO_2 without any intermediates is also part of the efforts of the academic community. At first, a tandem reaction was designed consisting of three steps: hydrogenation of CO_2 to FA (a); esterification to the formate ester (b); hydrogenation of the formate ester to methanol (c) [92]. The total TON for the whole cascade reaction was 2.5 in respect of methanol in a one-pot reaction (Fig. 2.9).

The direct hydrogenation of CO_2 was initially shown by the Leitner group while the hydrogenation to methanol is conducted within one catalytic cycle (Fig. 2.10).

The ligand triphos is the game-changer in this synthesis and in cooperation with the additives gives a TON for the ruthenium complex of 603. The activity of this catalyst system is comparable to the heterogeneous catalyst systems.

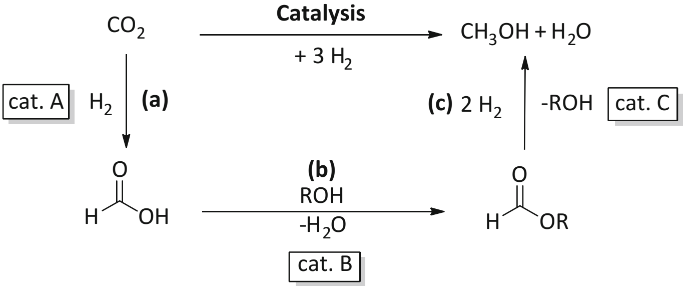


Fig. 2.9 Three-step tandem catalysis

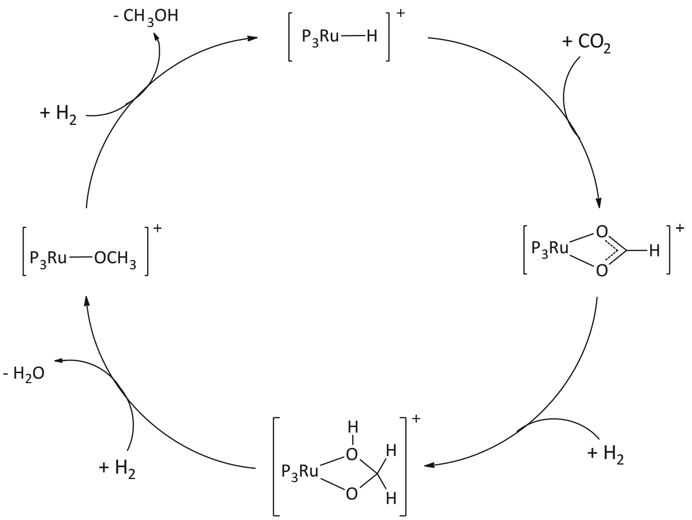


Fig. 2.10 MeOH production from direct catalytic hydrogenation of CO_2 and proposed mechanism

2.3 Lignin

As lignin is a complex three-dimensional amorphous polymer that consists of methoxylated phenylpropanoids (see Chap. 1.3.4), it is a hard task to generate valuable chemical products or products blends [93]. Since lignin is the only widespread renewable with aromatic moieties, several approaches were made to depolymerise lignin as alternative to the petrochemically produced aromatics [94, 95]. Hydrotreating is one possibility to produce chemicals with low molecular weight from lignin. These processes are also named hydrodeoxygenation, hydrogenation, and hydrogenolysis depending on the molecular structure to be cleaved. The monomers from lignin are usually linked by ether or by C–C bonds. The majority of almost two-thirds or more are ether bonds. The review of Zhang beautifully shows differences of the linkages (Fig. 2.11) [96].

The big challenge in the valorisation of lignin is the different linkages of the polymeric structure and the big variety of the compositions of lignin depending on plant type, part of the plant, etc. [97, 98].

The homogeneous-based systems for hydrogenation of lignin compounds are relatively rare in comparison with the heterogeneous catalyst systems [99]. Table 2.2 shows recent examples of homogeneous catalysts with model substrates. Only few catalyst systems are ready to work with processed lignin from, e.g., the Kraft process.

Hu hydrogenated lignin model compounds such as 4-propylphenol, eugenol, 1,2-dimethoxy-4-propylbenzene, and 2,6-dimethoxy-4-propylphenol at 298 K with a di-μ-chlorobis(η^4-1,5-hexadiene)-dirhodium(I) complex. In a solvent system of hexane/water, mostly double bond and the aromatic rings were hydrogenated. This

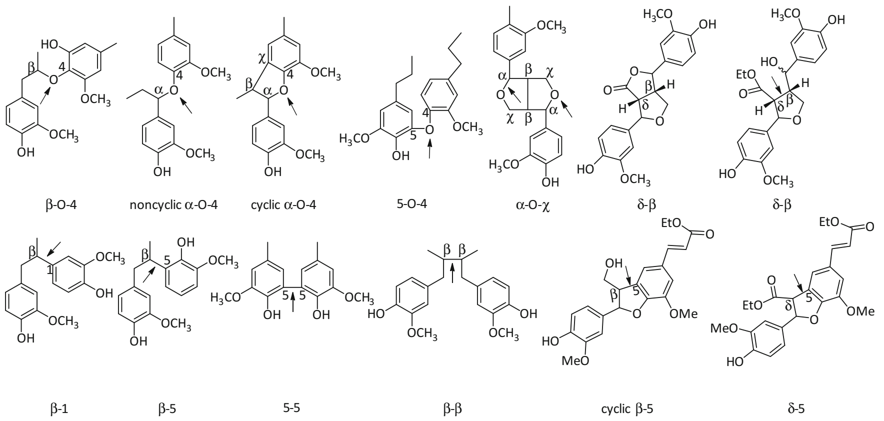


Fig. 2.11 Typical linkages between the primary units of lignin

reactivity is not beneficial due to the point that no cleavage has occurred and hydrogen has been consumed. Further examples used other model substrates, such as phenol, anisole, and anthracene [102–105, 108, 109].

The group of Nagy used besides Raney Ni, Pt/C, and $NaBH_4/I_2$ also the homogeneous hydrogenation catalyst $Ru(PPh_3)_3Cl_2$ in the hydrogenation of organosolv lignin in order to significantly reduce the molecular weight of the lignin. This catalyst was able to cleave 4-O-5- and aryl-O-aliphatic linkages to decrease oxygen content in the product mixture [106].

Nickel complexes with a N-heterocyclic carbene (SIPr·HCl) and NaOtBu as an additive are also active in the hydrogenolysis of diaryl ethers [107]. At 0.1 MPa, H_2 yields of 54–99% for the corresponding phenols and arenes were reported by Hartwig. The cleavage activity for aromatic C–O bonds of this system is in the order of Ar–OAr $\gg$ Ar–OMe > $ArCH_2$–OMe. Comparable heterogeneous Ni catalyst showed different selectivities to the diol instead of the phenol (Fig. 2.12) [110].

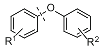
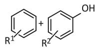
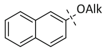
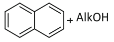
The group of Marks developed a nice way to process aliphatic ethers or furans with a tandem strategy of homogenous and heterogeneous catalysis. The homogeneous catalyst is a transition metal triflate that decyclises the C–O bond in the furan while the supported Pd nanoparticle catalyst hydrogenates the resulting double bond. This reaction is conducted in a stabilising IL and yields linear alcohols with no loss of any aromaticity (Fig. 2.13) [111, 112].

These reactivities are dedicated to cleave β-O-4 ethanol aryl ethers and do not affect the aromatic rings in the substrates [113, 114]. Popular catalyst systems are $Ru(Cl)_2(PPh_3)_3$, $RuH_2(CO)(PPh_3)_3$, and Ru-Xantphos, as shown in Fig. 2.14.

A new reactivity was lately shown by Leitner by addressing the C–C Bond in β-O-4-linked molecules. The Ru triphos complex showed again, as already shown in the CO_2 hydrogenation, a unique reactivity (Fig. 2.15) [115].

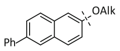
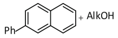
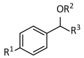
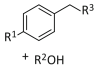
Different substrates were applied with high selectivities for the cleavage of the C-C bonds. These developments show the possibility to address several linkages in lignin by homogeneous catalysis.

Table 2.2 Homogeneous catalytic systems for the hydrogenation of lignin and their corresponding model substrates

	Reaction conditions							
Catalyst	*T* (K)	*P* (MPa)	*t* (min)/solvent	Substrate	Products	Conv. (%)	Notes	References
(1,5-hexadiene) RhCl dimer[a]	[f]	0.1	[g]	Phenol	cyclohexanol	[g]		[100]
Colloidal rhodium	[f]	5	[g]	Methylanisole	Methylcycohexane, 1-methyl-2-methoxycyclohexane[h] Mmethylcyclo-hexanone	100		[101]
[(1,5-C_6H_{10}) $RhCl]_2$[b]	[f]	0.1	3000	2-methoxy-4-propylphenol	*cis*-2-methoxy-*cis*-4-propylcyclohexanol, *cis*-2-methoxy-*trans*-4-propylcyclohexanol	100		[102]
Oxo-trirhodium (III)acetate[c]	313	0.1	[g]	Anthracene	1,2,3,4-tetrahydroanthracene, 1,2,3,4,5,6,7,8-octahydroanthracene	[g]	[i]	[103]
$[(C_6H_6)_4Ru_4H_4]Cl_2$[d]	363	6	14	Acetophenone	Methylcyclohexylketone, Phenylethanol, Cyclohexylethanol	64		[104]
$[(C_6H_6)_4Ru_4H_4]Cl_2$[d]	363	6	14	Anisole	Methoxycyclohexane	22		[104]
Rhodium nanoparticles[e]	348	4	600	4-methoxyphenol	4-methoxy-cyclohexanol, 1-methoxy-4-cyclohexenol	21		[105]
$RuCl_2(PPh_3)_3$	[f]	5	[g]	Ethanol organosolv lignin	Lower Mw lignin	[g]	[j]	[106]
$Ni(COD)_2$, SIPr• HCl	120	0.1	*m*-Xylene			>85	R=H, Me, *m*-OMe, CF_3	[107]
$Ni(COD)_2$, SIPr• HCl	120	0.1	*m*-Xylene			100	Alk=Hexyl, Me	[107]

(continued)

Table 2.2 (continued)

	Reaction conditions							
Catalyst	T (K)	P (MPa)	t (min)/solvent	Substrate	Products	Conv. (%)	Notes	References
Ni(COD)$_2$, SIPr• HCl	120	0.1	*m*-Xylene			85	Alk=Hexyl	[107]
Ni(COD)$_2$, SIPr• HCl	120	0.1	*m*-Xylene			>85	R^1=^{t}Bu, H; R^2=Ph, Me; R^3=H, Et	[107]

[a]With phase transfer catalyst. [b]With Bu$_4$NHSO$_4$ phase transfer agent. [c]Active after reduction with H$_2$. [d]Biphasic conditions. [e]In ionic liquids. [f]Room temperature. [g]Not specified. [h]Two isomers. [i]Extremely air sensitive. [j]More hydroxyl groups. SIPr*HCl = 1,3-Bis(2,6-diisopropylphenyl)imidazolidinium chloride

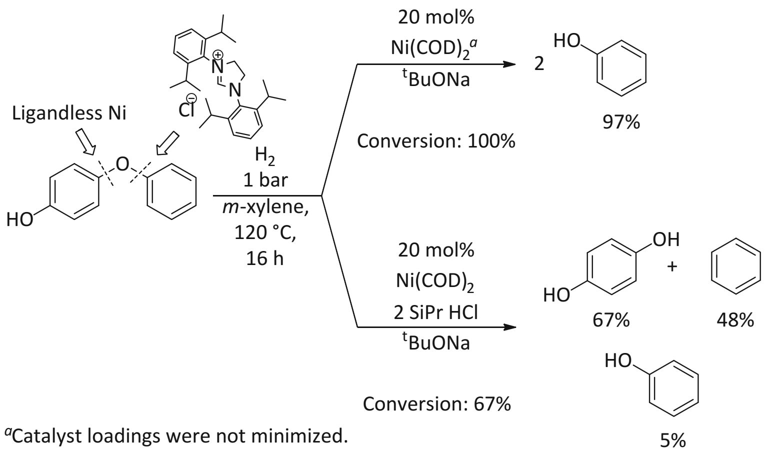


Fig. 2.12 Selectivities in nickel-catalysed hydrogenation

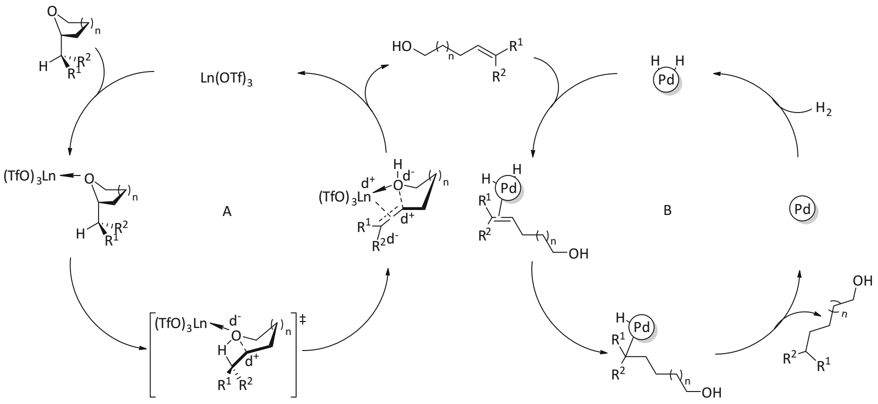


Fig. 2.13 Proposed tandem pathway for lanthanide triflate/Pd nanoparticle-mediated etheric C–O bond hydrogenolysis

2.4 Sugars

The conversion of cellulose, starch, or the corresponding oligo- and mono-sugars by hydrogenation with homogeneous catalysts is rarely reported. Hydrogenation of carbohydrates can be divided into the conversion of polymers into degraded products or monomers and further processed derivatives like HMF. The depolymerisation of cellulose is acid catalysed hydrogenolysis to fermentable sugars [116]. For the conversion of mono-sugars such as glucose in big scale processes to yield, e.g. the sweetener sorbitol, heterogeneous catalyst are used.

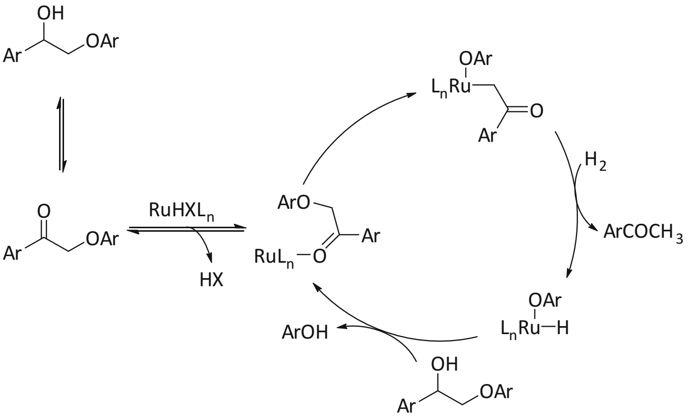


Fig. 2.14 Mechanism of Ru-catalysed C–O-bond cleavage of lignin-related polymers

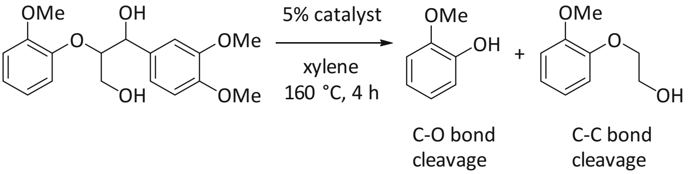


Fig. 2.15 Hydrogenation of lignin surrogate by Ru triphos

An example using homogeneous catalysis for depolymerisation was shown by Jiang to yield alcohols by applying 80–120 bar hydrogen with nickel salts. The intermediates glucose and xylose were hydrogenated in one pot to sorbitol and xylitol in yields up to 87.9% [117] (Fig. 2.16).

Furthermore, homogeneous reactions with platform intermediates from sugar are reported, as like HMF [118] to caprolactam. Also fragrances and pharmaceuticals can be synthesised incorporating homogenous catalysis [119].

2.5 Fats

The hydrogenation of unsaturated fats and oils is a well-established process in oleo chemistry and is called “hardening”. This process is used in the nutrition industry for producing margarine. Liquid unsaturated oils are converted into their corresponding saturated fats. The common catalyst for this process is Raney nickel, while some processes also use palladium particles [1]. A more challenging transformation is the selective conversion of polyunsaturated fatty acids into mono-unsaturated compounds (Fig. 2.17).

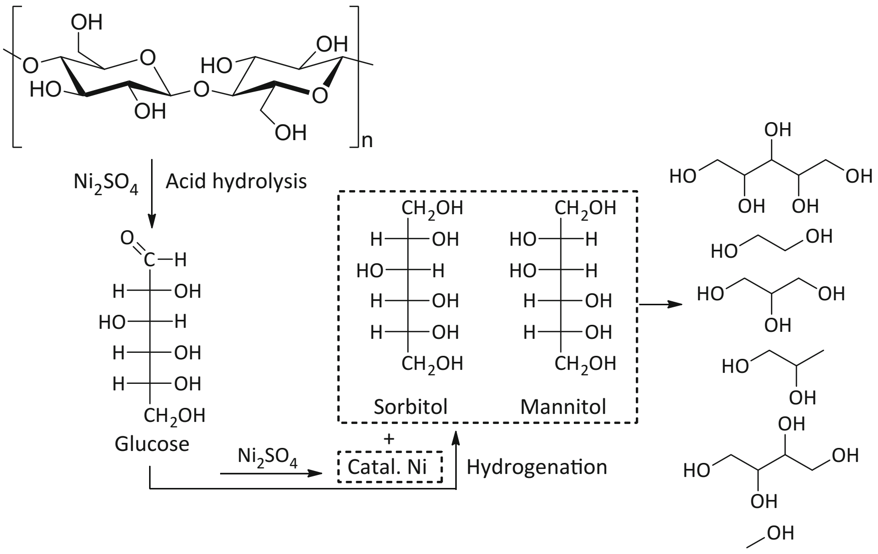


Fig. 2.16 Hydrogenation of cellulose to corresponding degradation products

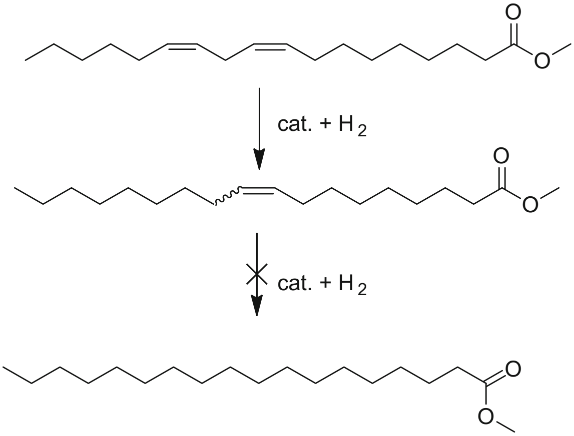


Fig. 2.17 Selective hydrogenation of methyl linoleate to C18:1—acid methyl ester

These reactions are catalysed by palladium carbonyls, platinum-tin systems, iron, and cobalt or nickel salts, which are activated by triethylaluminium [120–123]. Good results are observed with precious metal phosphine catalyst, for example, Wilkinson's catalyst [124]. High conversions of linoleic esters can be easily obtained with a palladium nanocatalyst. The catalytically active nanoparticles (diameter: 4 nm) are obtained by reducing palladium dichloride with hydrogen in DMF or propylene carbonate and an aqueous buffer. Sunflower oil with a linoleic acid content of 70% is converted into 92% oleic acid with no detectable content of linoleic acid. These palladium nanoparticles are also suitable for recycling using a liquid/liquid technique [125–127].

2.6 Conclusions

In conclusion, the hydrogenation of renewables with homogeneous catalyst addresses several points for future greener chemistry. The upgrade of raw renewable polymers such as lignin or sugars is of high importance to use more of these good available feedstocks. Furthermore also defined high value molecules can be yielded by hydrogenation of the renewables. Specially, the hydrogenation of CO_2 will gain more importance in the future as possible energy storage or as starting point for C_1-building blocks.

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Chapter 3
Hydroformylation of Renewables

Tom Gaide, Arno Behr and Andreas J. Vorholt

3.1 Introduction

The formal addition of a hydrogen atom and a formyl group to a double bond in the presence of a transition metal catalyst is called hydroformylation or oxo-synthesis. This reaction, discovered by Otto Roelen in 1938 during his investigations about the Fischer–Tropsch reaction, is one of the most important industrial applications of homogeneous catalysis [1]. In the year 2012, more than 12 million tons of hydroformylation products were synthesised [2]. A schematic hydroformylation of a terminal olefin is shown in Fig. 3.1.

The formyl group can be added to each of the double bond carbon atoms, yielding either in a linear (*n*-) or in a branched (*iso*-) aldehyde. Due to the rule of Keulemans, the formyl group is preferably added to the lower substituted carbon atom; thus, formation of the *n*-aldehyde is favoured [3].

While phosphine-modified complexes of cobalt and rhodium are, due to their high activity, the only catalysts applied in industrial processes yet, there are several transition metals as hydroformylation catalysts described in literature, e.g. ruthenium, palladium, iridium, platinum-tin [4]. In particular, ruthenium- and iridium-based catalysts become increasingly attractive due to the development of new ligands, which improve the activity of these catalysts [5, 6].

A detailed overview about the hydroformylation was recently published by Franke and Börner [7].

3.1.1 Mechanisms

A mechanism for cobalt-catalysed hydroformylation of olefins was developed by Heck and Breslow in the 1960s (Fig. 3.2) [8].

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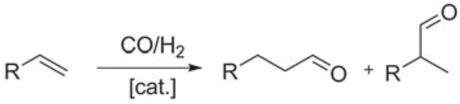


Fig. 3.1 Hydroformylation of a terminal olefin

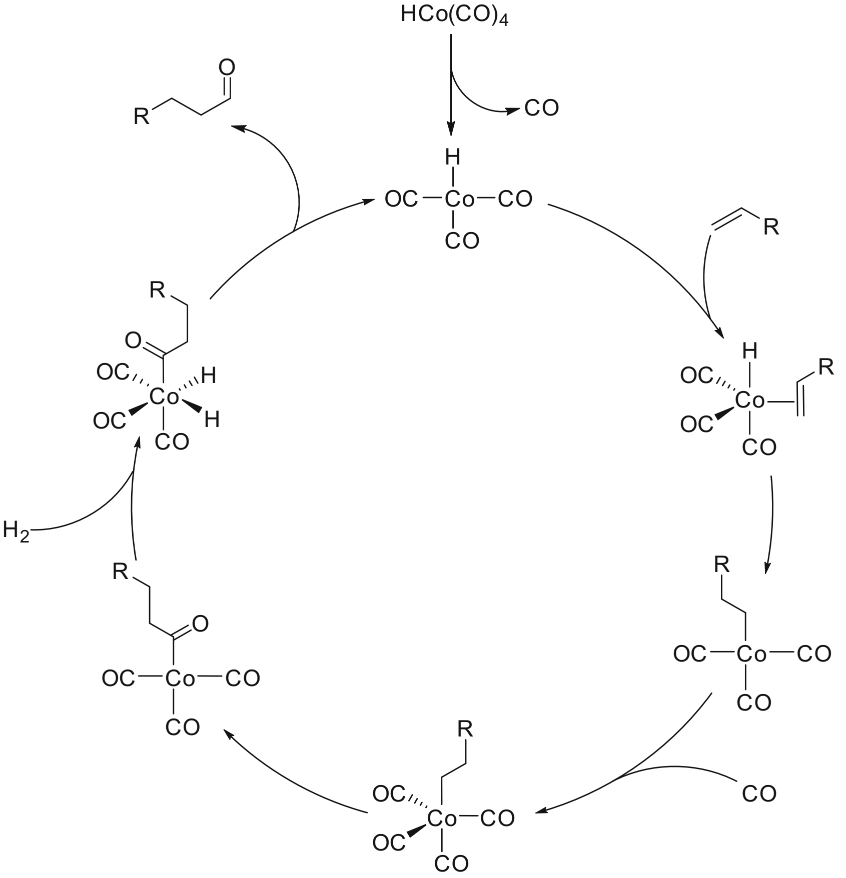


Fig. 3.2 Mechanism of the cobalt-catalysed hydroformylation

Starting from the cobalt (I) precursor tetracarbonylhydridocobalt, the active catalyst is formed by loss of one molecule carbon monoxide. The resulting tricarbonylhydridocobalt is able to associate an olefin, which undergoes insertion into the Co–H bond. This step determines whether the *n*-aldehyde or the *iso*-aldehyde is formed. After insertion in the Co–H bond, the complex associates a carbon monoxide molecule and insertion of carbon monoxide into the Co–alkyl bond

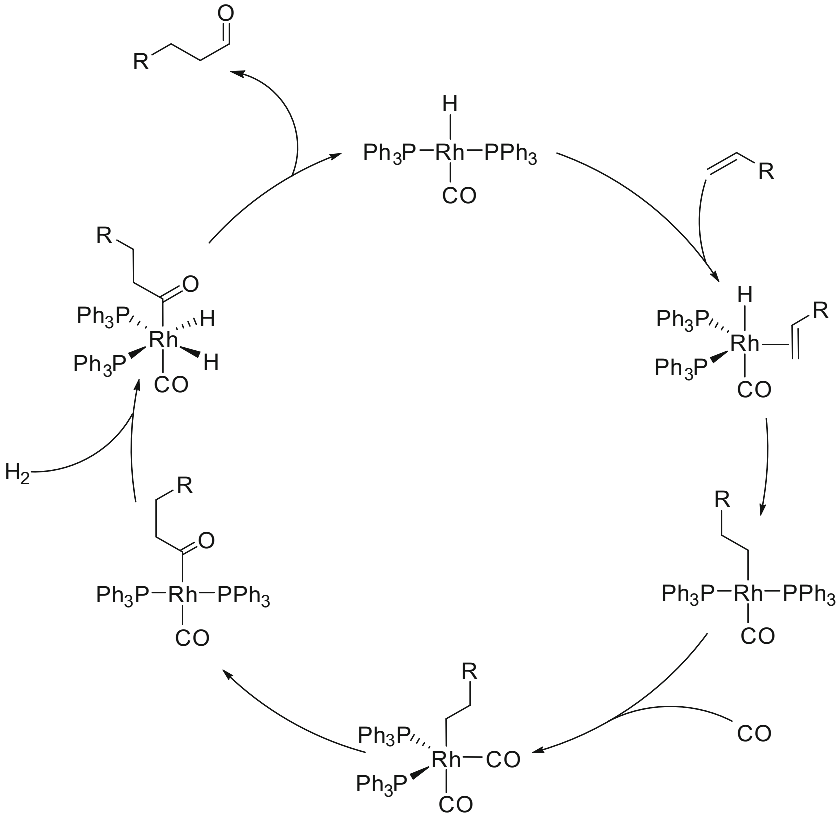


Fig. 3.3 Mechanism of the rhodium-catalysed hydroformylation

occurs. Finally, the oxidative addition of dihydrogen followed by reductive elimination of the free aldehyde under recovery of the active catalyst takes place.

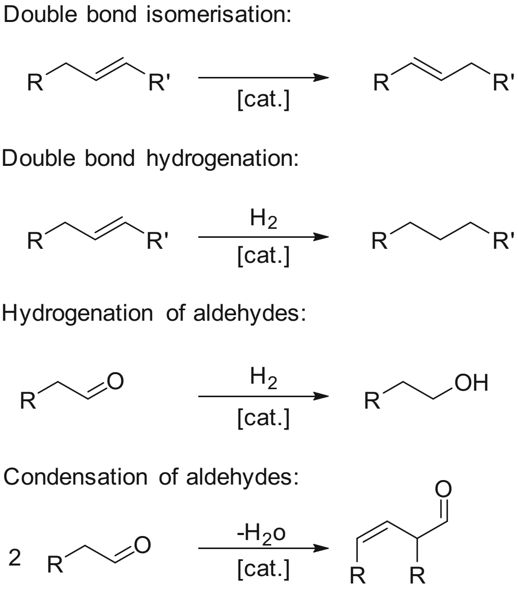
G. Wilkinson made a suggestion for a mechanism of the alkene hydroformylation by use of rhodium–phosphine complex catalysts (Fig. 3.3) [9].

The reaction steps proceed in the same sequence compared to the mechanism of the cobalt-catalysed hydroformylation, but by use of an additional phosphine ligand, there are many possible intermediates involving different number of phosphine ligands bonding to the rhodium or geometric arrangements [10].

3.1.2 Side Reactions

In the presence of a transition metal catalyst and synthesis gas, several side and consecutive reactions can occur. The most prominent side reactions are the

Fig. 3.4 Side reactions



hydrogenation and the isomerisation of the C=C double bond. Consecutively, resulting aldehydes can be reduced to the corresponding alcohols or undergo a condensation reaction (Fig. 3.4) [4].

Double bond isomerisation constitutes an interesting side reaction in hydroformylations. In respect of formation of linear aldehydes, isomerisation is boon and bane depending on the starting material. Starting from substrates with internal double bonds, linear aldehydes are available through double bond isomerisation to the end of the carbon chain and subsequent hydroformylation. If the starting material already contains a terminal double bond, isomerisation is disadvantageous and leads to formation of internal aldehydes or decelerates the reaction [11].

The hydrogenation of double bonds is an undesired side reaction, leading to loss of substrate to low-value chemicals and lower selectivity in hydroformylation (see Chap. 7).

Hydrogenation of nascent aldehydes can be used to synthesise corresponding alcohols in a tandem reaction [12]. This reaction can be either desired or not. On the one hand, alcohols are an important class of chemical intermediates and a tandem reaction consisting of hydroformylation and consecutive aldehyde reduction offers an easy access for them. Consequently, this reaction is implemented on industrial scale via the Shell process in which a phosphine-modified cobalt catalyst is used. On the other hand, aldehydes are straightforward convertible into further classes of chemical intermediates (e.g. carboxylic acids and amines). In this case, formation of aldehydes is undesired.

Condensation of two aldehydes is also described in literature. Again, this can be an interesting consecutive reaction for the synthesis of chemical intermediates. For

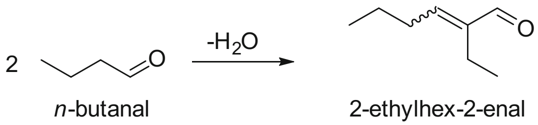


Fig. 3.5 Condensation of *n*-butanal

example, condensation of two molecules of *n*-butanal to 2-ethylhex-2-enal (Fig. 3.5) is a crucial reaction step for the synthesis of 2-ethylhexanol, which is an important intermediate in the syntheses of PVC plasticisers [13].

3.1.3 Catalyst Development in Industrial Hydroformylation Processes

In hydroformylation, several transition metals are suitable catalysts, e.g. rhodium, cobalt, ruthenium, iridium, and platinum-tin [6]. However, only cobalt and rhodium catalysts have gained industrial importance until today. The first hydroformylation, discovered by Otto Roelen, was realised with a cobalt catalyst as side product of Fischer–Tropsch experiments [2]. Cobalt catalysts require relative high pressures and temperatures for satisfying yields in hydroformylation. Rhodium as the most active catalyst metal enables hydroformylation under milder conditions compared to cobalt [4].

The industrial implementation of hydroformylation ensues in four steps. The first catalyst generation consists of unmodified cobalt carbonyl hydride complexes. Corresponding processes were developed by BASF and Exxon in the 1950s. In these processes, high pressures (200–300 bar) and temperatures between 110 and 180 °C are required. The cobalt catalyst was recycled via chemical precipitation.

In the second hydroformylation catalyst generation, catalyst relies on phosphine-modified cobalt catalysts and is applied in the Shell process. Corresponding alcohols are obtained as main products and a reduced synthesis gas pressure compared to the first catalyst generation (50–100 bar) is applicable. Separation of the catalyst is realised via product distillation after reaction.

In the 1970s, Union Carbide Corporation designed the low-pressure oxo (LPO)-process applying a rhodium–phosphine catalyst, which is referred to as the third catalyst generation, for hydroformylation under mild conditions (15–20 bar, 85–115 °C). The rhodium catalyst in the LPO process can be recycled either via gas or via liquid recycle. In the gas recycle process, the products are evaporated under process conditions. In the liquid recycle process, both the catalyst and the products leave the reactor as a liquid and the hydroformylation products are separated from the products via distillation.

The Ruhrchemie/Rhône-Poulenc process uses water-soluble phosphine-modified rhodium catalysts (fourth catalyst generation) in the hydroformylation of short chain olefins, enabling a straightforward catalyst recycling via phase separation after reaction. Hydroformylation with this technique is limited to short chain olefins due to poor solubility of higher olefins in water [4, 14].

3.2 Oleocompounds in Hydroformylation

The development of hydroformylation catalysts and catalyst recycling strategies was mainly focussed on the conversion of non-functionalised olefins based on petrochemicals. Indeed, the hydroformylation is also applicable to renewable feedstocks that contain naturally C=C double bonds. In comparison with substrates based on petro chemicals, oleocompounds usually contain one or more internal double bonds and an additional functional group (e.g. carboxylic acid and ester). The implementation of renewables in industrial chemistry is of great interest due to the shortage of fossil resources and their volatile prices. The hydroformylation of oleocompounds offers access to interesting intermediates for the polymer, lubricant, or surfactant industry [15].

3.2.1 Catalyst Development

First investigations of hydroformylation with unsaturated oleocompounds were carried out by Natta et al. using a cobalt/iron catalyst on a bentonite support to transform methyl oleate, olive oil, and grape-stone oil into the corresponding aldehydes. Under 110 °C and 10–20 bar synthesis gas, they mainly obtained branched aldehydes as products. Heating the reaction mixture up to 140 °C results in the formation of the corresponding alcohols [16].

16 years later, Ucciani et al. investigated the homogeneously catalysed hydroformylation of unsaturated fatty acid esters. They used cobalt laurate and $Co_2(CO)_8$ as catalyst precursors in the conversion of methyl oleate under high syngas pressures (240–310 bar) and temperatures between 175 and 190 °C (Fig. 3.6). Resulting, branched aldehydes are immediately reduced to the corresponding alcohols under these conditions [17].

The hydroformylation of methyl oleate, methyl linolate, methyl linoleate, soybean oil, safflower oil methyl esters, and linseed oil methyl esters by use of cobalt catalysts was also investigated by Frankel et al. While at 100 °C the formation of aldehydes in yields up to 84% is observed, higher temperatures lead to subsequent hydrogenation of resulting aldehydes to corresponding alcohols. The use of tributylphosphine as additional ligand leads to formation of linear oxo-products due to the higher activity in double bond isomerisation of the modified cobalt catalyst [18].

The first rhodium-catalysed hydroformylation of oleocompounds (methyl oleate in this case) was also reported by Frankel et al. In contrast to cobalt-catalysed hydroformylations, double bond isomerisation can be suppressed by use of rhodium

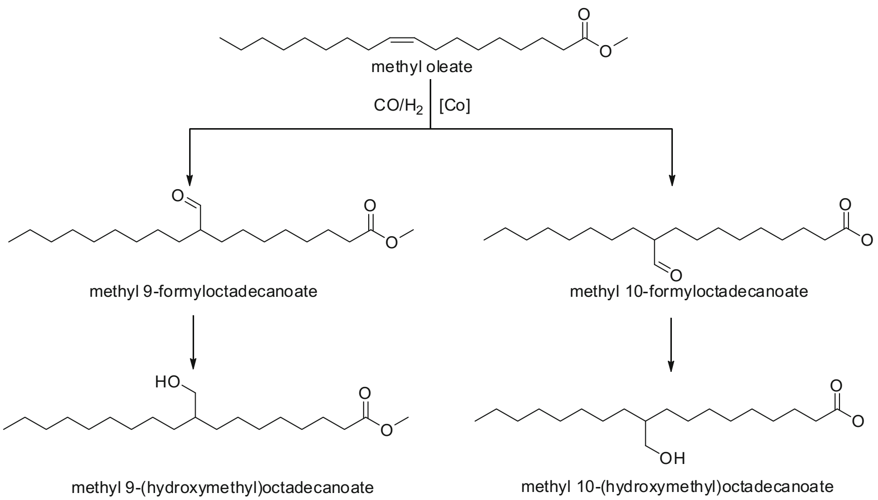


Fig. 3.6 Cobalt-catalysed hydroformylation of methyl oleate

with triphenylphosphine as additional ligand. This leads to a hydroformylation mainly in position 9 and 10 of the carbon chain (yield up to 99%, selectivity towards hydroformylation in position 9 and 10 >80%) [19].

A comparison of rhodium and cobalt catalysts shows that rhodium has a higher activity in hydroformylation under lower pressures and temperatures. Furthermore, rhodium catalysts are less active in double bond isomerisation under operating conditions.

Technical-grade fatty acid esters and triglycerides (methyl oleate and soybean oil in this case) are also suitable starting material in hydroformylation reactions. If [$RhH(CO)(PPh_3)_3$] with additional triphenylphosphine is used as catalyst, yields for the aldehyde of up to 91% are observed under mild conditions (100 °C and 40 bar) [20].

Kinetic studies of the hydroformylation of oleocompounds with rhodium catalysts were carried out by Kandanarachchi et al. [21]. If triglycerides (soybean oil, high oleic safflower oil, safflower oil, and linseed oil) are used as substrate, the reactivity seems to be independent of the type of used triglyceride and if the triglyceride contains multiple unsaturated fatty acids. In contrast, free fatty acid methyl esters or fatty acids containing two or three double bonds are less reactive than monoolefins due to the formation of a π–allyl complex leading to an inactive rhodium complex. In the hydroformylation of soybean oil influences of temperature, syngas pressure and substrate concentration were investigated. The reaction rate increases with higher temperatures until 100 °C. Further temperature increase leads to formation of phosphido-bridged dimeric rhodium clusters which are catalytic inactive. An increasing total syngas pressure ($CO/H_2 = 1/1$) leads to higher reaction rates. For the substrate concentration, a first-order dependence was estimated. Also the effect of the ligands triphenylphosphine and triphenylphosphite was examined. The activation

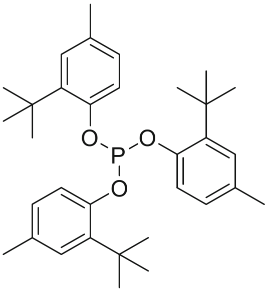


Fig. 3.7 *Tris*-(2-*tert*-butyl-4-methylphenyl) phosphite

energy for the hydroformylation of soybean oil in the presence of triphenylphosphine is lower (66.1 kJ/mol) compared to triphenylphosphite (77.4 kJ/mol) resulting in a higher activity of the rhodium/triphenylphosphine catalyst system.

Several investigations regarding different ligands in rhodium-catalysed hydroformylation of oleocompounds were conducted. Van Leeuwen and co-workers [22] used bulky phosphite-modified rhodium catalysts in the hydroformylation of methyl oleate. These catalysts allow higher turnover frequencies (400–500 h^{-1}) under moderate conditions (100 °C and 20 bar syngas) compared to phosphines like triphenylphosphine. If technical methyl oleate, containing 14% 9, 12-diene methyl linoleate, is used as substrate, the reaction rate is lower due to the formation of the already mentioned π–allyl intermediates. Figure 3.7 shows *tris*-(2-*tert*-butyl-4-methylphenyl)phosphite which was applied as ligand.

Börner et al. [23] applied several lactam-based phosphoramidite ligands in the rhodium-catalysed hydroformylation of methyl oleate. Under mild conditions (80 °C and 30 bar syngas pressure), hydroformylation occurs with high chemoselectivities up to 99%. The best performance is achieved with a ligand based on a four-membered lactam ring (Fig. 3.8). This ligand is also the most stable towards water compared to the other tested ligands [23].

The application of alternative catalyst metals is also an interesting field of research in the hydroformylation of oleocompounds. Carpentier et al. [24–26] published detailed studies regarding the application of Rh, Ir, Pd, and Ru as catalyst metal in combination with the biphephos ligand in the hydroformylation of terminal unsaturated 10-undecenitril (Fig. 3.9).

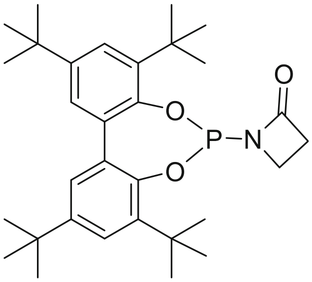


Fig. 3.8 Phosphoramidite ligand [23]

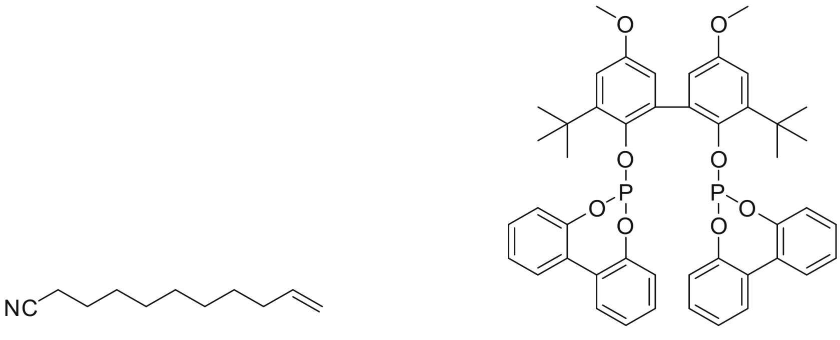

10-undecenitril
biphephos

Fig. 3.9 10-undecenitril and biphephos ligand

Table 3.1 Comparison of different metals in the hydroformylation of oleocompounds [24–26]

Catalyst metal	Price ($/oz) [27]	TOF (h^{-1})	S_{aldehyde} (%)	*l/b*	TTON
Rh	765	3320	88	99/1	250.000
Pd	735	210	76	99/1	Not recycled
Ir	675	770	75	99/1	58.000
Ru	40	310	76	99/1	55.000

While a rhodium catalyst provides highest catalyst activity (TOF 3320 h^{-1}), chemo selectivity (S_{aldehyde} 88%), and productivity (total turnover number (TTON) 250.000), excellent regio selectivities (*l/b* 99/1) can be achieved with all applied catalyst metals (Table 3.1). With the exception of the palladium complex, all catalysts can be recycled by high vacuum distillation. In particular the Ru/biphephos catalyst seems to be a very attractive alternative since nowadays, the price for Ru is about 20 times lower compared to Rh [27].

3.2.2 Catalyst Recycling

In homogeneous catalysed hydroformylation, the catalyst recovery often is a great challenge in order to design an economic feasible process. In principle, a homogenous catalyst can be separated from the product by different approaches such as distillation, extraction, or catalyst immobilisation on solid or liquid carriers.

Catalyst recycling concepts on industrial-scale hydroformylation, which were already described in Sect. 4.1, are designed for the conversion of unfunctionalised, relatively short-chained olefins. Resulting oxo-products have relatively low polarity and low boiling points. In the hydroformylation of oleo compounds, these methods are often not applicable, since resulting products have high boiling points and contain an additional functional group compared to oxo-products gained from

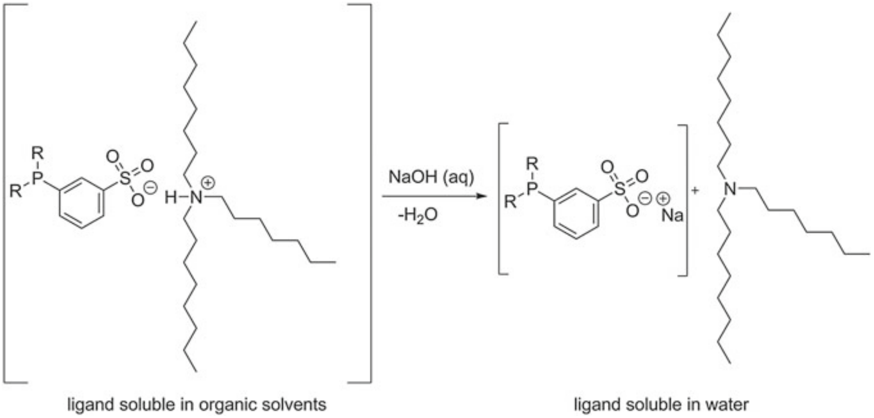


Fig. 3.10 Switchable ligand for the catalyst extraction in hydroformylations

short-chained olefins. For this reason, there are many affords to find suitable catalyst recycling strategies in literature.

Bahrmann et al. [28] used sulfonated aromatic phosphine ligands in combination with rhodium precursors in the hydroformylation of oleyl alcohol. Coupling sulfonate groups on the ligand with long-chained ammonium groups offers access to rhodium-ligand complexes which are soluble in organic solvents like toluene. Reaction takes place under 100–170 °C and 100–450 bar syngas pressure. After reaction, the solution is treated with aqueous sodium hydroxide solution leading to loss of the ligands ammonium counter ions. In consequence, the catalyst complex gets soluble in water and can be separated from the product phase via extraction with water (Fig. 3.10). The catalyst can be regenerated by treatment with mineral acids and subsequent extraction with ammonium containing toluene.

Recently, Monflier et al. [29] reported about the application of naturally occurring cyclodextrins as supramolecular emulsifiers in the hydroformylation of triglycerides in water. The substrate and the cyclodextrins form a supramolecular complex, which allows the interaction between the substrate and the water-soluble Rh/TPPTS (TPPTS = trisulfonated triphenylphosphine) catalyst. With this system, yields of the desired aldehyde of 74% after 6 h are reached. Stopping stirring the reaction mixture after reaction induces the separation of the aqueous catalyst phase and the product phase. The catalyst phase was reused three times without significant loss of activity, which demonstrates the applicability of this elegant approach.

Another approach for hydroformylation of oleocompounds is the micellar two-phase catalysis. This technique uses surfactants to take the hydrophobic substrates into the aqueous catalyst containing phase. Fell et al. [30] determined the influence of several surfactants. In particular, cationic and amphoteric detergents provide promising results in the hydroformylation of methyl 10-undecenoate, which is available from pyrolytic cleavage of ricinoleic acid (Fig. 3.11). With this system, it is possible to generate more than 90% formyl products after three hours with 0.5 mol% rhodium and 30 mol% sulfonated triphenylphosphine in water. Without

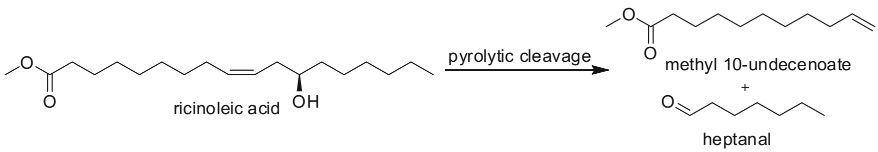


Fig. 3.11 Pyrolytic cleavage of ricinoleic acid

surfactants, a quantitative conversion of methyl 10-undecenoate in aqueous media was only achieved after 20 h. Furthermore, the multiple hydroformylation of linolenic acid methyl ester and linseed oil is possible with micellar two-phase catalysis.

Also activated charcoal was tested as mass transfer additive for the hydroformylation of methyl oleate in water. Sulfonated triphenylphosphine in combination with a rhodium precursor was used as catalyst in these investigations. After 24 h, the yield of oxo-products is up to 93% under relatively mild conditions in water. Monflier et al. [31] were able to show that there is no loss of catalyst activity within two recycles. The concentration of rhodium and phosphorus in the product phase is less than 0.2 ppm. Further substrates such as technical-grade methyl oleate, methyl 10-undecenoate, or linolenic acid methyl ester are also convertible into oxo-products in high yields with this technique.

Catalyst immobilisation can also be received by use of ionic liquids instead of water as solvent for the catalyst. Suarez et al. [32] examined this approach for a rhodium recycle in hydroformylation of soybean oil. Their reaction system enables quantitative yields for oxo-products applying 100 °C and 40 bar syngas pressure after 8 h if triphenylphosphine is used as additional ligand. Compared to a reaction without ionic liquids, a higher selectivity can be reached in the presence of an ionic liquid due to a catalyst stabilising effect. In the absence of triphenylphosphine, the reaction is distinctly slower, and after 24 h, formation of rhodium nanoparticles is observed. Unfortunately, the loss of rhodium into the product phase is very high (about 20%).

Thinking of industrial applications catalyst stability is an important point. Tulchinsky et al. [33] designed a new class of sulfonated water-soluble phosphine ligands without aryl–phosphorus bonds. Ligands containing aryl–phosphorus bonds tend undergoing alkyl–aryl exchanges through reaction of the phosphine ligand with olefins. Due to the elimination of the possibility of aryl–alkyl exchange, these ligands are pretend to have an improved stability and catalyst life time. Use of the corresponding rhodium complexes leads to aldehyde yields up to 80% in the hydroformylation of soybean methyl esters. Figure 3.12 shows three examples of these ligands.

A process concept for a hydroformylation of oleocompounds with subsequent extraction of the catalyst was developed by Dow Technologies (Fig. 3.13) [34, 35]. The concept is based on water-soluble sulfonated phosphine-modified rhodium catalyst. The first step is a non-aqueous hydroformylation of the starting material. For this reaction, an organic solubilising agent for the catalyst is necessary. This can

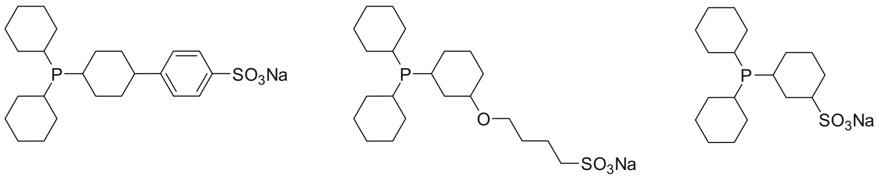


Fig. 3.12 Water-soluble ligands without aryl–phosphorus bonds

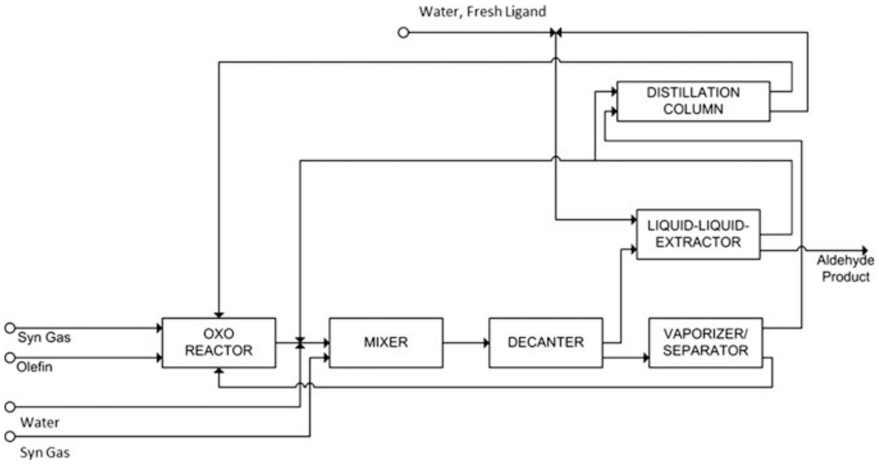


Fig. 3.13 Process concept for the hydroformylation of oleocompounds [34, 35]

be polar, an organic solvent such as *N*-methyl-2-pyrrolidone or *N*,*N*-dimethylformamide. After reaction, an extraction with water is executed in order to separate the catalyst from the product. After phase separation, the water in the catalyst phase is removed via distillation and the catalyst can be recycled into the reactor. The rhodium concentration in the product phase is lower than 1 ppm.

Recently, our group reported about a new process concept for the conversion of fatty compounds in aqueous thermomorphic solvent systems (TMS-systems). TMS-systems take advantage of the temperature dependent miscibility of a polar, catalyst containing solvent and a non-polar, substrate/product containing solvent. Heating up theses mixtures lead to the formation of one single phase and the reaction takes place homogeneously without mass transport limitations. Cooling down after reaction induces phase separation and the catalyst can be separated from the product via simple decantation. The hydroformylation of methyl 10-undecenoate was chosen as model reaction. The use of a thermomorphic solvent system consisting of water and 1-butanol in combination with a water-soluble rhodium/SulfoXantphos (sulfonated bidentate xantphos-type ligand) catalyst enables very high turnover frequencies of 1500 h^{-1} and a highly regio selective reaction towards the linear hydroformylation product (89%). The catalyst was reusable in three recycling runs. The reaction was also transferred into a continuously operated miniplant to show the applicability of this system for technical approaches (see Sect. 11.3) [36].

3.2.3 Applications

Usually, hydroformylation products are not used directly but are converted to more stable and useful bifunctional molecules. Figure 3.14 shows the most common consecutive reactions of hydroformylation products of oleocompounds (see also Chap. 7 for tandem reactions).

Table 3.2 gives an overview about application possibilities of hydroformylated oleocompounds.

Polyhydroformylated triglycerides are mostly hydrogenated to corresponding polyols (Fig. 3.15) [37].

Hydrogenation can be executed either in a one-step process by cobalt-catalysed tandem hydroformylation/hydrogenation sequence or in a two-step process through rhodium-catalysed hydroformylation followed by hydrogenation of resulting aldehydes with Raney nickel. Resulting polyols are used for polyurethane synthesis. Cobalt-catalysed hydroformylation/hydrogenation leads to lower yields of polyols compared to rhodium/nickel catalysis due to double bond isomerisation. Corresponding polyurethanes have different properties. If polyols are synthesised with rhodium/nickel, resulting polyurethanes are rigid. Hard polyurethane rubbers with lower mechanical strength are obtained if cobalt catalysts are applied for polyol synthesis. Often, fatty acid methyl esters are used as substrate for alcohol synthesis. Polymers based on alcohols from oleocompounds can be used for foams, adhesives, elastomers, coatings, and mastics.

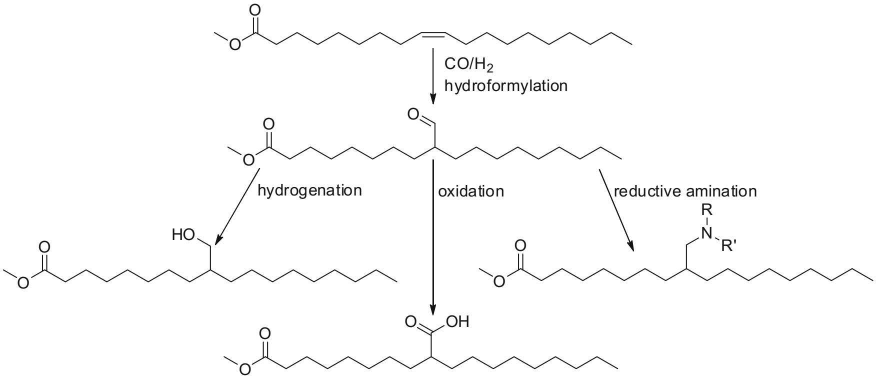


Fig. 3.14 Consecutive reactions of hydroformylated oleocompounds

Table 3.2 Possible applications for hydroformylated oleocompounds

Substrate	Consecutive reaction	Application
Polyhydroformylated triglycerides	Reduction to the corresponding alcohols	Synthesis of polyurethanes
Polyhydroformylated triglycerides, polyhydroformylated fatty acids or methyl esters	Reductive amination	Building blocks for polyamide synthesis
Polyhydroformylated triglycerides, polyhydroformylated fatty acids or methyl esters	Oxidation to the carboxylic acid and subsequent esterification	Lubricants
polyhydroformylated fatty acids or methyl esters	Reduction to the corresponding alcohols and subsequent esterification with acetic anhydride	Plasticisers

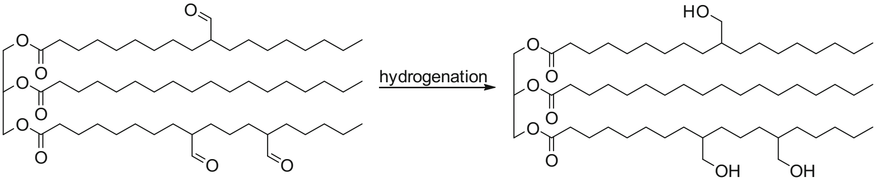
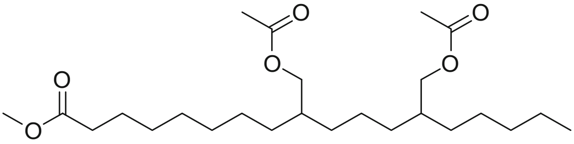


Fig. 3.15 Example of the synthesis of polyols from hydroformylated triglyceride

Fig. 3.16 Bio-based plasticiser



Besides polyols, polyamines are synthesised via consecutive reductive amination or hydroaminomethylation of fatty esters, which can be monomers for polyamides. Oxidation of aldehydes to carboxylic acids enables access to polyesters or polyamides.

Hydroformylation of fatty acids or fatty esters allows introduction of side groups in order to gain attractive lubricants. Besides their low toxicity, these bio-based lubricants have several benefits compared to oil-based lubricants such as higher viscosity index, lower volatility, or higher fire resistance.

The product in Fig. 3.16 obtained by esterification of hydroformylated/hydrogenated linolic acid methyl ester with acetic acid is a well-suited plasticiser with higher heat stability and higher tensile strength compared to phthalate diesters. A more detailed overview can be found in the review of Monflier et al. [37].

3.3 Terpenes and Naturally Occurring Allylbenzenes

Terpenes and naturally occurring allyl benzenes are a promising renewable olefin source. Their good availability and reasonable price make them attractive as raw material for further functionalisation (see Sect. 1.2). Hydroformylated terpenes can be applied in perfume, flavour, surfactant, or pharmaceutical chemistry. Also use as chiral building blocks is thinkable [38].

3.3.1 Catalyst Development

Clement et al. [39] compared the reactivity of several terpenes with different substituted double bonds and conjugated double bonds (Fig. 3.17) in cobalt-catalysed hydroformylation. They also investigated the influence of the solvents hexane, methanol and 6% aqueous acetone at 150 °C and 250 bar syngas pressure.

Table 3.3 shows the relative reaction rates of the terpenes in different solvents, while the reaction rate of α-pinene in hexane is assigned a value of one.

Limonene shows high hydroformylation activity in all tested solvents. The activity of α-pinene in methanol and 6% aqueous acetone is comparable to limonene. Myrcene and α-terpinene are less active due to their conjugated double bonds which can form less active π–allyl complexes with cobalt. In all cases, complex product mixtures containing alkanes, alcohols, and high boilers are obtained. Multiple hydroformylation was not observed at all.

Himmele and Siegel [40] studied the hydroformylation of α- and β-pinene with rhodium and cobalt catalysts. By use of a cobalt catalysts, (-)-α-pinene is converted to (-)-2-formylbornane (Fig. 3.18) under relative harsh conditions (120 °C, 300 bar). Use of (+)-α-pinene leads to formation of (+)-2-formylbornane.

Rearrangement of the ring structure from the α-pinene to the bornane structure is ascribed to the presence of acidic hydridocarbonyl cobalt species under hydroformylation conditions. If rhodium is used as catalyst, no rearrangement to bornane structure is observed, but an isomerisation of the double bond can occur leading to addition of the formyl group to the outstanding methylene substituent (Fig. 3.19).

The ratio of the products depends on applied pressure ratio of CO and H_2 and temperature. While higher temperatures (110 °C), high pressures (650 bar), and high CO/H_2 ratios (70/30) shift the product spectrum towards A (Fig. 3.19), lower

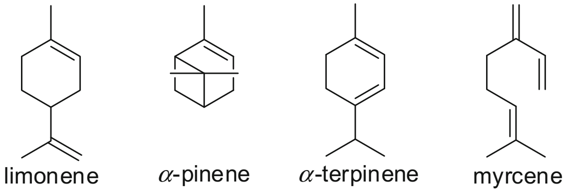


Fig. 3.17 Terpenes (investigated by Clement [39])

Table 3.3 Comparison of the reaction rates of several terpenes in hydroformylation [39]

	Hexane	Methanol	6% aqueous acetone
α-pinene	1.0	5.0	4.8
Limonene	5.6	4.8	4.2
α-terpinene	0.3	0.5	0.3
Myrcene	1.1	2.3	0.3

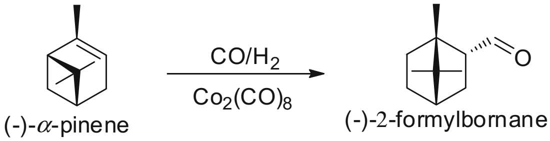


Fig. 3.18 Cobalt-catalysed hydroformylation of (-)-α-pinene

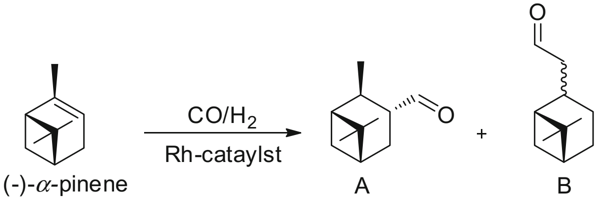


Fig. 3.19 Rhodium-catalysed hydroformylation of (-)-α-pinene

temperatures (70 °C), lower pressures (350 bar), and lower CO/H_2-ratios (50/50) lead to higher amounts of B.

Hydroformylation of limonene (Fig. 3.20) with phosphine- and phosphite-modified rhodium catalysts under mild conditions (90 °C, 14 bar) was reported by van Leeuwen and Robeek [41]. Comparison of different ligands shows strong enhanced catalyst activity in the presence of tris(*o*-*tert*-butylphenyl)phosphite (3.500 h^{-1}) compared to triphenylphosphine (100 h^{-1}).

Chalchat et al. tested several monoterpenes and sesquiterpenes in rhodium-catalysed hydroformylation under relatively mild conditions. Yields of the hydroformylation products are in the range of 25 and 82% depending in the nature of the terpene (e.g. see Fig. 3.21) [42].

Fig. 3.20 Limonene hydroformylation

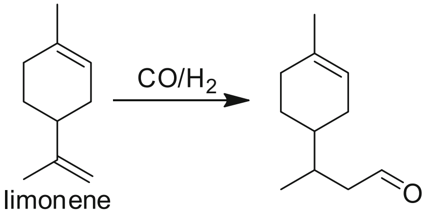


Fig. 3.21 Terpene hydroformylation from Chalchat et al.

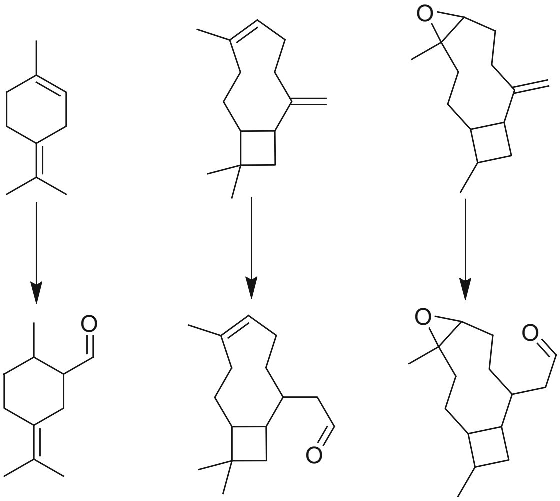
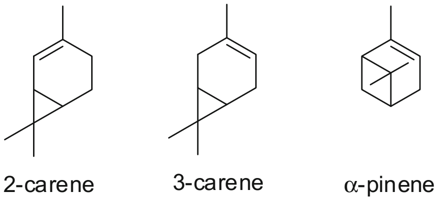


Fig. 3.22 Examples for sterically encumbered double bonds in terpenes



Hydroformylation of sterically encumbered trisubstituted endocyclic double bonds of terpenes (Fig. 3.22) is a particular challenge.

Dos Santos et al. [43] investigated the influence of different phosphine and phosphite ligands in rhodium-catalysed hydroformylation of these terpenes. If unmodified rhodium precursors are used as catalysts, a high double bond isomerisation rate is observed which leads to complex mixture of alcohols and aldehydes. In the presence of ligands such as triphenylphosphine or triphenylphosphite in high P/Rh ratio (20/1), isomerisation was suppressed but activity in hydroformylation decreases dramatically. This circumstance is traced back to formation of rhodium complexes containing two or three ligands. These complexes are not very active in hydroformylation of these substrates. In contrast, if the bulky phosphite ligand $P(O\text{-}o\text{-}{}^{t}BuPh)_3$ is used, double bond isomerisation is reduced and a relatively high activity in hydroformylation is observed even with high P/Rh ratio of 20/1. Due to ligands large cone angle rhodium complexes containing only one ligand are mainly formed.

If monoterpenic multiple unsaturated olefins are used as substrates, conjugation of double bonds leads to a different activity for hydroformylation. In case of myrcene, uncommon effects in terms of reaction conditions are observed. High concentrations of ligand, high basicity of ligand, and high pressures of CO and H_2

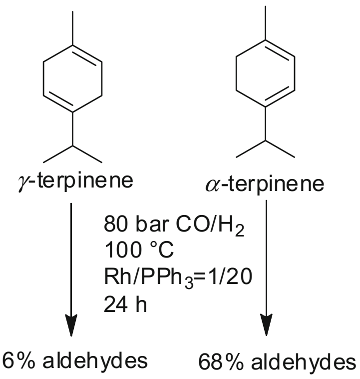


Fig. 3.23 Monoterpenic endocyclic dienes

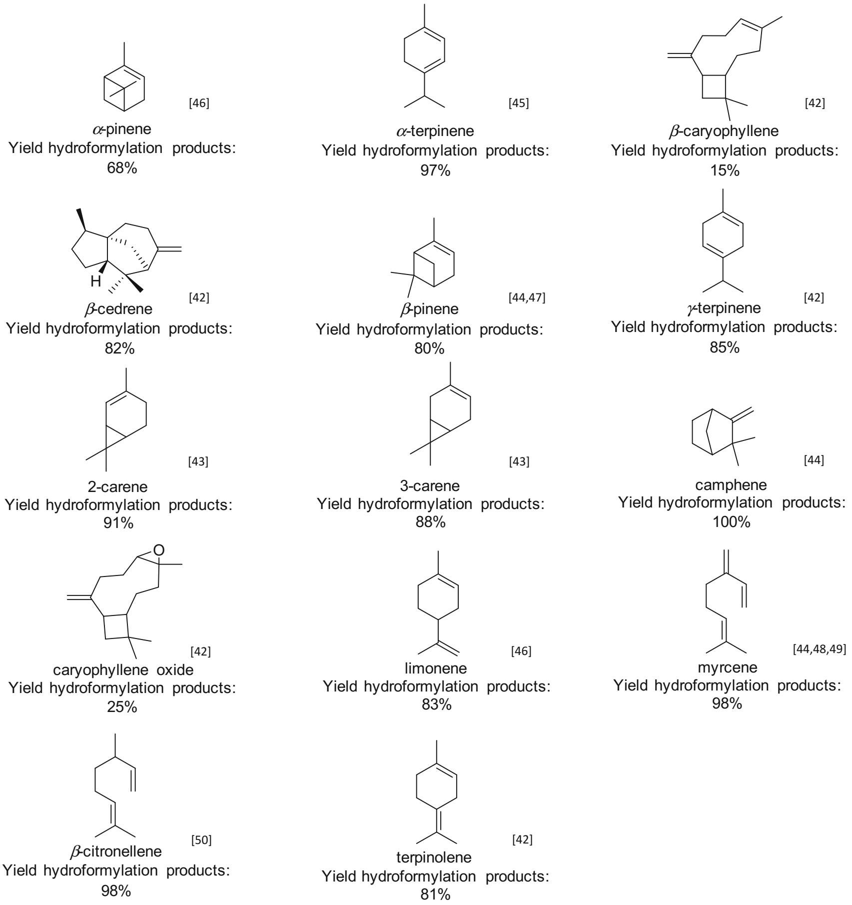


Fig. 3.24 Hydroformylation of estragole

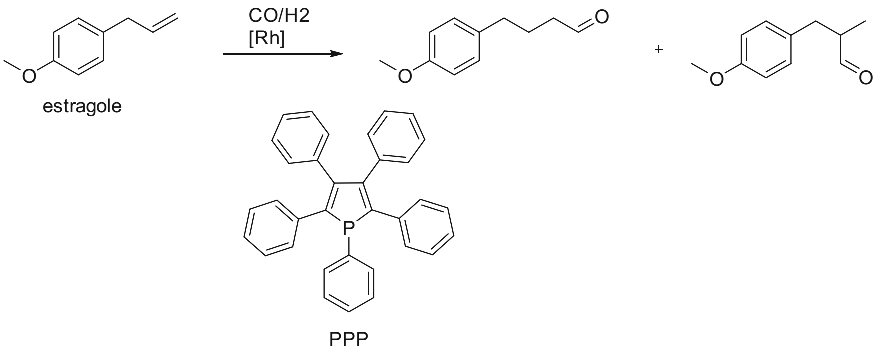


Fig. 3.25 Overview of the hydroformylation of several terpenes

accelerate the hydroformylation reaction. These results lead to the assumption that conversion of less active η^3-allyrhodium intermediates into η^1-complexes is a critical step in myrcene hydroformylation. This effect is not observed if endocyclic conjugated dienes like α-terpinene are used as substrate. Non-conjugated monoterpenic endocyclic dienes are less reactive compared to conjugated ones (Fig. 3.23) [44, 45].

Figure 3.24 gives an overview about the hydroformylation of several terpenic substrates.

Also the hydroformylation of naturally occurring allylbenzenes leads to interesting products. Dos Santos et al. investigated the ligand influence in the rhodium-catalysed hydroformylation of estragole (Fig. 3.25). By application phosophole ligand PPP (Fig. 3.25), the regio selectivity for hydroformylation in the terminal position is 78% (aldehyde yield 96%). Similar results are obtained with triphenylphosphine (regio selectivity 75%; aldehyde yield 97%) (Fig 3.24).

Thinking of applications for functionalised terpenes in perfume or pharmaceutical industry, stereo- and diastereoselective hydroformylation is from great interest. In this context, Kóllar and co-workers [51] examined the hydroformylation of chiral terpenes (+)-*R*-limonene and (-)-*R*-carvone with platinum/tin catalysts and bidentate phosphine ligands (Fig. 3.26). Diastereoselectivity is controllable by choice of ligand. Highest selectivities towards one diastereomer are observed by using a catalyst system consisting of $PtCl_2$((+)-bdpp) and $SnCl_2$.

Kóllar also compared rhodium and platinum/tin catalysts in asymmetric hydroformylation of several mono- and sesquiterpenes. In all cases, rhodium catalysts provide higher activities in hydroformylation while platinum/tin system is slightly more diastereoselective. The nature of the hydroformylated substrate has a high influence on stereoselectivity. Bicyclic terpenes provide distinctly higher diastereoselectivities. Best results are obtained if (+)-β-cedrene is converted with a $[Rh(NBD)Cl]_2/PPh_3$ catalyst system (Fig. 3.27) [52].

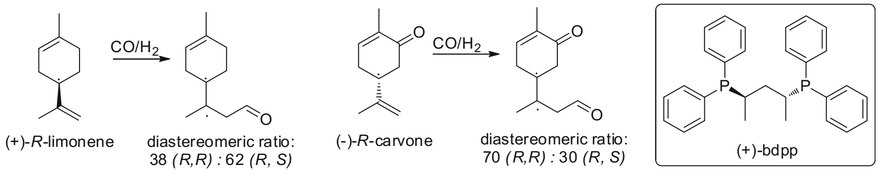


Fig. 3.26 Diastereoselective hydroformylation with Pt/Sn catalysts

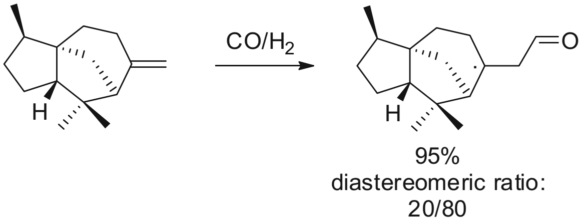


Fig. 3.27 Rhodium-catalysed hydroformylation of (+)-*β*-cedrene

High diastereoselectivities in hydroformylation of (+)-*β*-pinene (up to 99%) and camphene (up to 82%) are reached if bimetallic cobalt/rhodium or platinum/tin catalysts are used at 100 °C and 60 bar [48, 53].

3.3.2 *Catalyst Recycling*

Catalyst recycling in terpene and allyl benzene hydroformylation is a challenging task. Due to the high boiling points of the hydroformylation products, separation via distillation in the presence of the catalyst can induce formation of by products or catalyst deactivation. Consequently, alternative catalyst recycling strategies like catalyst immobilisation in liquid phase or on a solid carrier have to be applied to regain the valuable catalyst.

Dos Santos and co-workers [54] pursued the approach of aqueous biphasic hydroformylation as a recycling concept in terpene hydroformylation. Resulting product phase can easily be separated by simple decantation after reaction. Toluene is used as non-polar solvent and additionally the cationic surfactant cetyltrimethylammonium chloride (CTAC, Fig. 3.28) is used as phase transfer

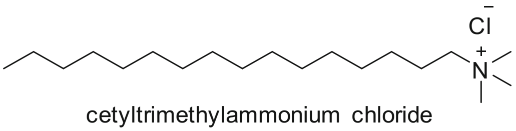


Fig. 3.28 Cetyltrimethylammonium chloride (CTAC)

agent. A water-soluble sulfonated triphenylphosphine-modified rhodium complex is utilised as catalyst.

The authors determined coherence between nature of the terpene and required amount of surfactant. For conversion of myrcene with the additive CTAC, a strongly promoting effect in hydroformylation is described. In the presence of CTAC in a concentration of 25 mM, a conversion of 96% is observed. Without surfactant, no reaction is observed. For limonene, lower CTAC concentrations of 2.5 mM appear to be optimal under applied conditions resulting in a conversion of 86%. In case of camphene as substrate, CTAC even causes an inhibition in hydroformylation. Best results of 71% conversion are obtained in the absence of surfactant. In a later study, scope was extended to citronellene [55].

The biphasic hydroformylation of different naturally occurring allylbenzenes was done by Baricelli et al. [56]. A mixture of toluene and water was used as reaction medium in combination with CTAC as phase transfer agent. For the conversion of eugenol, estragole, safrole, and *trans*-anethole (Fig. 3.29), rhodium and ruthenium catalysts modified with TPPTS or TPPMS (monosulfonated triphenylphosphine) were applied. Reaction performances of both ligands in rhodium-catalysed hydroformylations are comparable, although TPPMS leads to slightly higher chemo selectivity for the hydroformylation. High aldehyde yields in the hydroformylation of eugenol (92%), estragole (72%), and safrole (70%) are obtained with rhodium catalysts. Aldehyde yield in the conversion of *trans*-anethole (31%) is lower due to its internal double bond. If ruthenium is used as catalyst metal, harsher conditions are necessary (100 °C and 62 bar instead of 80 °C and 20 bar). While results in the Ru-catalysed conversion of eugenol are comparable to the ones achieved with rhodium catalysts, conversion rates of safrole, estragole and anethole are lower. The rhodium catalyst can be recycled four times. In case of ruthenium, the catalyst activity in the first recycling experiment was even higher compared to that of the initial run, because the catalytically active species is already

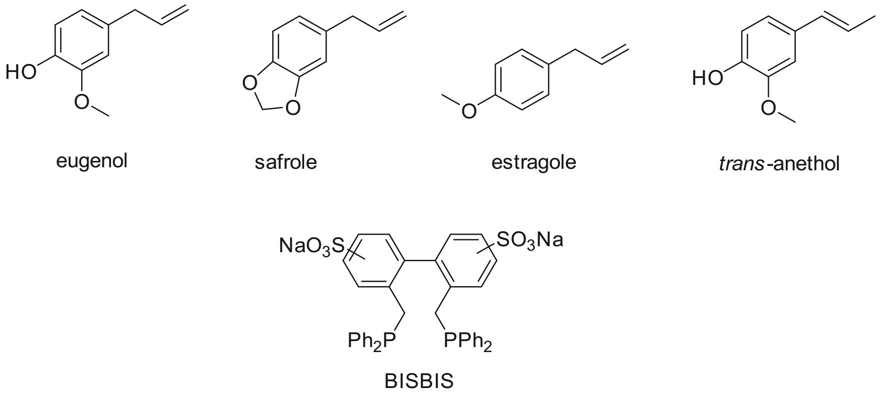


Fig. 3.29 Different allylbenzenes in biphasic hydroformylation [56]

formed in the recycling experiment. Unfortunately, a second catalyst recycle was not possible.

Application of bidentate ligands in rhodium-catalysed hydroformylation of these substrates in biphasic mixtures strongly influences the regio selectivity in this reaction [57]. If BISBIS is applied, regio selectivity in the hydroformylation is up to 92%.

Dos Santos et al. [58] also investigated catalyst immobilisation on a solid support. They anchored a rhodium/TPPMS catalyst complex in a commercially available anion exchange resin. This catalyst shows reactivity comparable to conventional homogeneous rhodium systems in the hydroformylation of eugenol and estragole and can be reused several times.

3.4 Conclusions

Oleocompounds and terpenes are attractive renewbale starting materials in hydroformylation reactions, and resulting products have interesting properties and a wide application area. For industrial applications, robust processes have to be developed. In particular, recycling of the expensive noble metal catalysts and long catalyst life times have to be guaranteed for an economic hydroformylation process. Several good approaches are already been made, but all approaches lack an application in a continuous set-up.

Resulting aldehydes often are useful intermediates. If consecutive reactions can be realised in effective tandem reaction sequences including the hydroformylation step, application of hydroformylation of renewables can gain importance for industrial applications due to reduction of production costs (e.g. lower investment costs if only one reactor is needed, no costs for purification of intermediates). Hydroaminomethylation, for example, could be an elegant way to synthesise surfactant precursors if terpenes are used as substrates or polymer precursors if fatty acids are the starting material.

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Chapter 4
Amination of Renewables

S. Fuchs, H. Warmeling, Arno Behr and Andreas J. Vorholt

4.1 Introduction

Aminations are a class of reactions in which an amino group is introduced into a target molecule to form amines or their derivatives. The industrial synthesis of amines is a field with high economic significance for the processing industry covering large-scale applications such as polymers, special chemicals, and pharmaceuticals [1, 2]. Besides heterogeneous catalysts, like zeolites, and homogeneous catalysts, such as Brønstedt acids or bases, the homogeneous transition metal catalysts are of high interest [3]. The most commonly used transition metals are gold, silver, palladium, platinum, rhodium, iridium, rhenium, and ruthenium [4]. One classic access to primary amines is the hydrogenation of nitriles, like in the production of adiponitrile from the DuPont process for the production of hexamethylenediamine, which is widely applied but suffers from low atom economy [5]. Alternative more atom efficient routes for the synthesis of amines are the direct C–N bond linkage (see Fig. 4.1) starting from alkenes [3], alkynes [3], dienes [6], and the condensation of the nitrogen substrates with alcohols [7], aldehydes [8], or halocarbons [9]. As a nitrogen source ammonia, primary and secondary amines or other nitrogen-containing molecules such as carbamates or amides can be utilised [4]. In this chapter, an overview about amination reactions is given involving renewable resources mentioned in the literature rounded with a conclusion of today's applications of aminations for renewable feedstocks. The content is arranged based on the substance class of the feedstock covering carbohydrates, fats and oils, and finally terpenes. From natural resources, derived substrates are also listed within this framework. Although amines can also be synthesised with hydroaminomethylation and telomerisation reactions these reactions are discussed in detail in the Chaps. 7 and 5, respectively.

The direct addition of amines to unsaturated compounds, such as alkenes, alkynes, or dienes, is referred to as **hydroamination**. Its catalytic cycle is shown in Fig. 4.2 for the amination of an olefin and a linear product. Potential catalysts for

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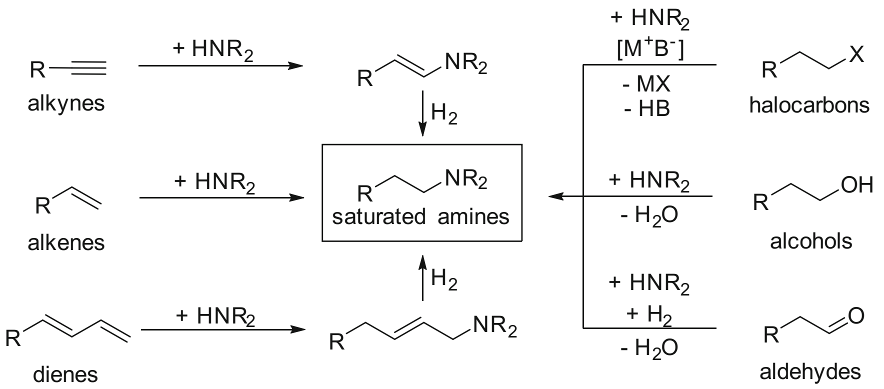


Fig. 4.1 Synthesis of amines from different functionalised substrates

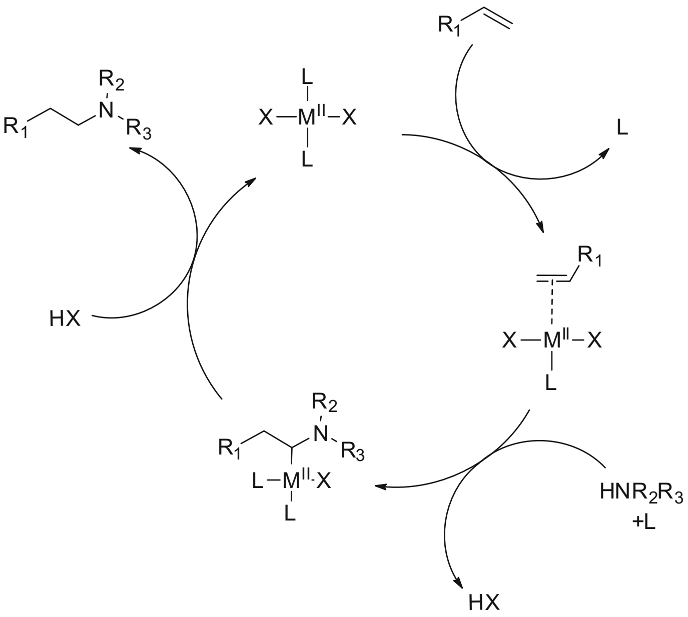


Fig. 4.2 Catalysis cycle of the hydroamination (olefinic substrate)

this transformation comprise heterogeneous as well as homogeneous systems. In comparison to *O*-nucleophiles, such as water or alcohols, the direct addition of amines to non-activated unsaturated compounds, although exothermic, is known to be difficult [3]. Nevertheless, a number of iridium and rhodium complexes are active in the direct amination of alkenes [10], and lanthanide or copper/silver catalysts have been used for the intramolecular hydroamination of single bonds [11].

Additionally, palladium-based systems can be used also for the synthesis of chiral products [12].

In contrast to non-activated substrates, hydroamination of conjugated double bond systems such as in 1, 3-butadiene [13], isoprene [14], or the renewable terpene myrcene [15] proceeds smoothly with high yields [16]. Palladium-based systems with monodentate phosphine or carbene ligands are appropriate catalysts. A broad substrate spectrum as *N*–nucleophiles has been realised (e.g. amides, carbamates, aromatic amines, and simple dialkylamines, e.g. diethylamine), giving rise to numerous interesting functional groups [17].

Alkynes can be transformed to the corresponding amines via hydroamination with subsequent hydrogenation of the intermediate enamines (Schiff's bases). With ruthenium, rhodium, gold, or titanium catalysts, different classes of amines are accessible, depending on the nature of the amine substrate (secondary, primary amine, or ammonia) [18, 19].

Alcohols, aldehydes, and halocarbons are large-scale easy accessible chemical intermediates. Hence, the production of amines from these intermediates is of considerable industrial as well as academic interest. Homogenous transition metal catalysis has been identified as the key for selective and atom economic transformation, represented by numerous systems that have been developed for the amination of, e.g., alcohols [20]. The very challenging formation of primary amines via amination of alcohols with ammonia has recently been addressed by several groups. Selectivity issues are caused by the high activity of the resulting primary and secondary amines in this type of reaction [21]. Therefore, tertiary amines are easily yielded with iridium-based catalysts, whereas higher selectivities towards primary amines can be obtained with ruthenium pincer complexes [22, 23]. The reaction proceeds via dehydrogenation of the alcohol to the aldehyde, with subsequent imine formation by condensation and final reduction of the imine [24].

Consequently, due to the described pathway, the reductive amination of aldehydes suffers the same selectivity issues, if primary or secondary amines are the desired products. Their nucleophilicity in comparison with, e.g., ammonia is enhanced, which results in the formation of higher substituted amines [25]. If the reductive amination of aldehydes is merged with a preliminary hydroformylation of alkenes, the tandem catalytic system is called hydroaminomethylation, which is discussed later on in Chap. 7 [26].

Halocarbons as substrates for chemical transformations are available on a large scale and benefit from the feature, that halides in general are good leaving groups. Hence, the formation of amines from aryl halides is feasible with, e.g., the palladium-catalysed Buchwald–Hartwig reaction [27]. The E-factor of these transformations is high, as high waste production by formation of halide salts cannot be prevented.

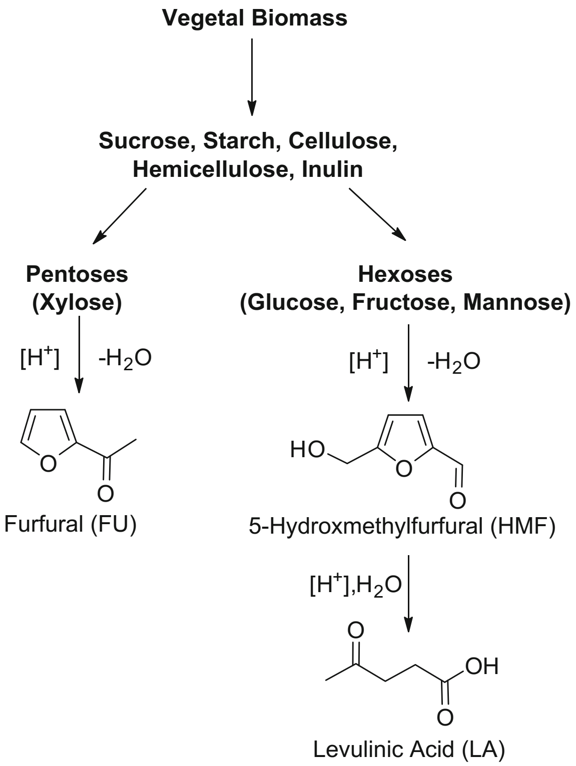


Fig. 4.3 From biomass to versatile building blocks by dehydration of carbohydrates (Corma et al. [28])

4.2 Carbohydrates

By simple thermal dehydration reactions under acidic conditions, the three building blocks furfural (FU), 5-hydroxymethylfurfural (HMF), and levulinic acid (LA) can be obtained from sugars, cellulose, hemicellulose, and inulin as can be seen in Fig. 4.3 [28, 29]. Through exchange of oxygen groups with amino groups platform chemicals like pyrrolidones are available for the production of various fine chemicals, polymers, and biofuels [30].

While the reductive amination of carbohydrates using stoichiometric amounts of sodium borohydride (Borch reagent, see Fig. 4.4) is well described in the literature [31–34], this chapter focuses on homogenous transition metal complex catalysis.

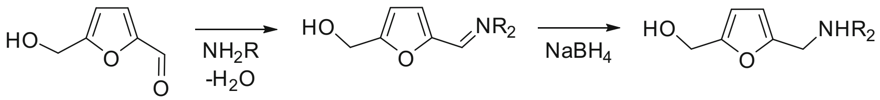


Fig. 4.4 Reductive amination of HMF using $NaBH_4$ in stoichiometric amounts [31]

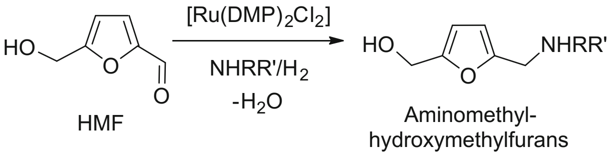


Fig. 4.5 Ruthenium-catalysed reductive amination of HMF to aminomethyl-hydroxymethylfurans

4.2.1 5-Hydroxymethylfurfural (HMF)

5-Hydroxymethylfurfural is listed as one of the top 10 biomass derived platform chemicals according to the US Department of Energy and is used as a bio-derived base for various fine chemicals, polymers, fuels, and pharmaceutical compounds as well as for other intermediates like levulinic acid which will be discussed later in this chapter [34].

In a direct reductive amination reaction, various aminomethyl-hydroxyfurfural compounds can be synthesised. The pharmaceutical activities of such amino HMF derivatives are well known and sufficiently documented in the literature. Medical applications are, e.g., muscarinic receptor antagonists, *Pyricularia oryzae* inhibitors, calcium antagonists, or cholinergic agents [35, 36].

These pharmaceuticals can be produced by Mannich-type reactions or two-step reductive aminations using sodium borohydride (see Fig. 4.4) from furfural alcohol or HMF, respectively. These reactions usually require harsh reactions conditions or cost intensive amination reagents [34].

To overcome these unfavourable reaction routes, several homogenous transition metal catalysts were investigated. Xu et al. found the ruthenium-based catalyst complex dichlorobis(2,9-dimethyl-1,10-phenanthroline)ruthenium(II) ($Ru(DMP)_2Cl_2$) to be highly efficient in reductive amination and to perform the conversion to high yields under mild conditions and without the formation of waste (see Fig. 4.5).

Tables 4.1 and 4.2 show the obtained results for various primary and secondary amine substrates and the applied reaction conditions.

4.2.2 Levulinic Acid

Levulinic acid (LA) is one of the most promising future chemical building blocks for post-fossil resource age. Being available by simple acidic dehydration of carbohydrates LA can be produced in large-scale quantities from non-edible and renewable biomass feedstocks [28, 29].

Levulinic acid can be catalytically converted into γ-valerolactone (GVL) which was also identified as a potential renewable platform chemical (see Fig. 4.6) [37].

Table 4.1 Results of the ruthenium-catalysed direct reductive amination of HMF with various primary amines

Entry (–)	R (substrates) (–)	Time (h)	Yield (%)
1	benzyl	5	93
2	4-OMe-benzyl	5	89
3	*o*-Me-benzyl	4	43
4[a]	*m*-Me-benzyl	4	90
5	*p*-ME-benzyl	4	91
6	4-F-benzyl	20	94
7	4-Cl-benzyl	20	95
8	4-Br-benzyl	20	95
9	4-CO_2Et-benzyl	24	69[a]
10	4-COMe-benzyl	20	66[a]
11	4-CN-benzyl	24	0[a]
12	4-$CONH_2$-benzyl	24	0[a]
13	6-aminoinole	5	58[b]
14	2-aminopyridine	20	0
15	Butylamine	20	0

Conditions: $T = 60$ °C, $n_{\mathrm{HMF}} = 0.5$ mmol, $n_{\mathrm{S}} = 0.55$ mmol, $p_{\mathrm{H_2}} = 12$ bar, LM: EtOH, $V_{\mathrm{LM}} = 1$ ml, cat: (Ru(DMP)$_2$CL$_2$), $c_{\mathrm{cat}} = 0.5$ mol%

[a] $T = 80$ °C

[b] Imine yield given

Table 4.2 Results of the ruthenium catalysed direct reductive amination of HMF with various secondary amines

Entry (–)	Amine (–)	Time (h)	Yield (%)
1	Morpholine	6	83
2	Dibutylamine	5	67
3	N-methylbenzylamine	6	79
4[a]	N-Methylanilin	6	79
5	N-Benzylaniline	19	74

Conditions: $T = 60$ °C, $n_{\mathrm{HMF}} = 0.5$ mmol, $n_{\mathrm{S}} = 0.55$ mmol, $p_{\mathrm{H_2}} = 12$ bar, LM: EtOH, $V_{\mathrm{LM}} = 1$ ml, cat: (Ru(DMP)$_2$CL$_2$), $c_{\mathrm{cat}} = 0.5$ mol%

[a] $T = 30$ °C

Hence, the nitrogen-containing derivatives pyrrolidones offer a high potential as an intermediate in fine chemical, polymer, and fuel production (see Fig. 4.6) [38].

Pyrrolidones are produced from LA by reductive amination using formic acid (FA) as a hydrogen transfer agent and is shown in Fig. 4.7.

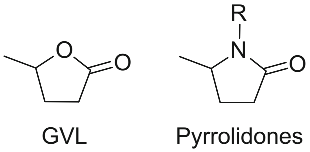


Fig. 4.6 γ-Valerolaceton (GVL) and pyrrolidones

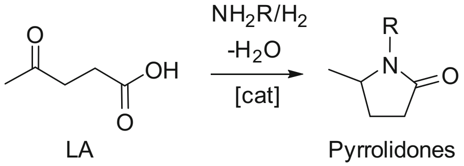


Fig. 4.7 Reductive amination of levulinic acid to pyrrolidones [30]

So far only the followingly discussed catalytic systems are known to perform the reaction with high yields [30].

While Du et al. [38] achieved high catalyst performance (Y = 88–97%) with a heterogeneous gold catalyst on zirconium support, Huang et al. applied a homogenous ruthenium catalyst (Precursor = [dichloro(*p*-cymene)ruthenium(II)]) with different phosphor ligands (Fig. 4.8 L1-6) and obtained good results at mild conditions. Here, ligand L4 leads to the best results with yields of 95 and 72% for benzyl and phenyl moieties. Formic acid (FA) is used as an in situ hydrogen source under aqueous conditions to carry out the hydrogenation of the imine or enamine species. Temperatures up to 120 °C were used at a catalyst loading of 0.5 mol% of LA concentration and an equimolar feed mixture of LA, formic acid, and nitrogen substrate.

Based on the work of Huang et al., Wei et al. found an efficient catalysis utilising cyclometallic iridium complexes (see Fig. 4.9). It is able to perform the reaction at even milder reaction conditions. Summarised results can be found in Table 4.3. The group also proposed a mechanism for the iridium-catalysed reductive amination of levulinic acid as depicted in Fig. 4.10. The catalytically active species is an iridium hydride complex that is formed in situ under acidic conditions from the iridicycle catalyst precursor [30].

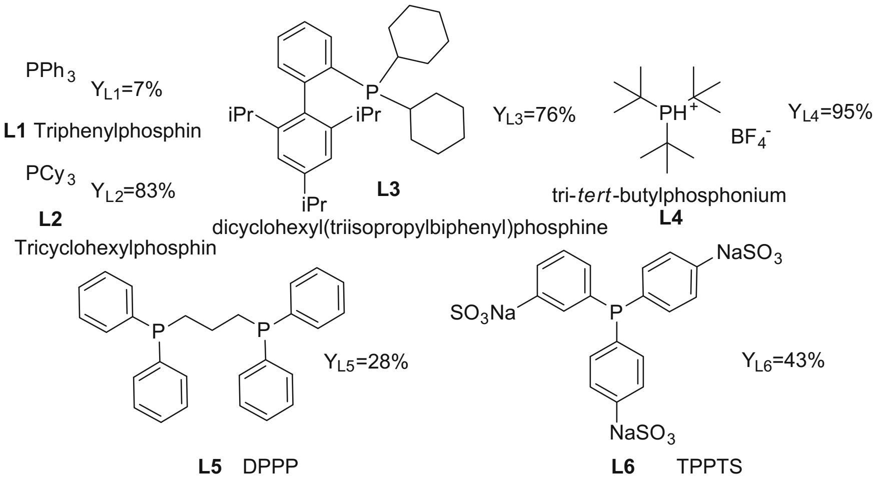


Fig. 4.8 Phosphorus ligands for the homogenous catalysed reductive amination of LA [39]

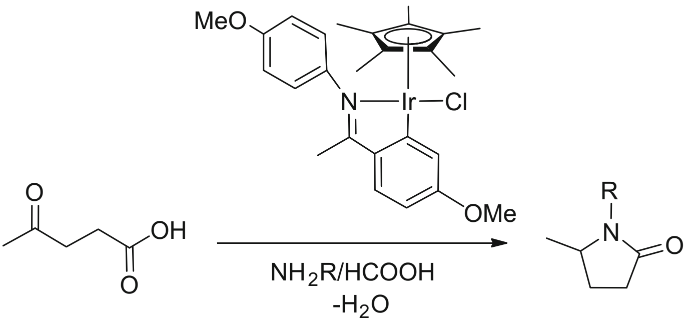


Fig. 4.9 Mild reductive amination of levulinic acid with various nitrogen substrates catalysed by cyclometallic iridium complexes [30]

Table 4.3 Results of the reductive amination of levulinic acid (Wei et al. [30])

Entry (–)	R (substrates) (–)	Time (h)	Yield (%)
1	Benzyl	4	86
2	4-OMe-benzyl	4	94
3	3-OMe-benzyl	12	94
4[a]	2-OMe-benzyl	24	96
5	3,4-OME-benzyl	24	94
6	4-F-benzyl	12	91
7[b]	*n*-Octyl	12	88

Conditions: $T = 80$ °C, $n_{\mathrm{LA}} = 3.2$ mmol, $n_{\mathrm{S}} = 8.6$ mmol, LM: Aqueous formic acid solution, $V_{\mathrm{LM}} = 3$ ml, $n_{\mathrm{FA}} = 14.5$ mol, pH = 3.5, $c_{\mathrm{cat}} = 0.1$ mol%

[a] $c_{\mathrm{cat}} = 0.5$ mol%

[b] pH = 4.5 and $c_{\mathrm{cat}} = 0.2$ mol%

4.2.3 Oils and Fats—Fatty Acid Esters

Renewable natural oils and fats are due to their chemical resemblance with fossil hydrocarbons, one of the most important and frequently used renewable raw materials. Plant oils are used not only for synthesis of diverse fine chemicals, but also for polymer chemistry [40].

Functionalised fatty acids such as epoxy ring containing fatty acids like internal epoxy fatty acid methyl esters (methyl epoxy stearate) are frequently used as starting material for the synthesis of *β*-amino alcohols, which are often applied in the synthesis of various biodegradable derivatives. Singh et al. report the synthesis of several *β*-amino alcohols by the epoxy ring opening reactions of methyl epoxy stearate. As catalyst zinc perchlorate hexahydrate [$Zn(ClO_4)_2 \cdot 6\ H_2O$], a weak Lewis acid catalyst was used (see Fig. 4.11). In the presence of this catalyst, the internal epoxy fatty acid methyl ester methyl 9,10-epoxyoctadecanoate in a solvent-free reaction with

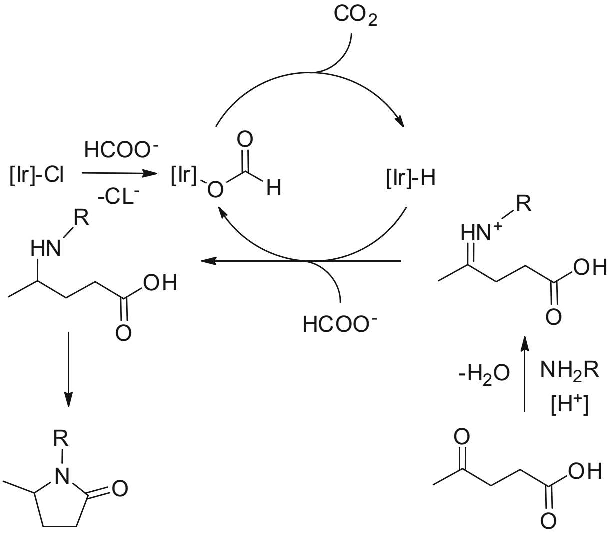
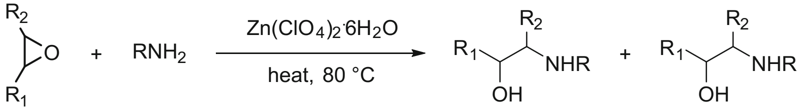


Fig. 4.10 Mechanism of the iridium catalysed reductive amination of levulinic acid (Wei et al. [30])



R=C_4H_9-(butyl), C_8H_{17}-(octyl), C_4H_8-(pyrrolidine), C_5H_{10}-(piperidine), C_4H_8O-(morpholine), C_6H_4-Cl(p-chloroaniline), C_6H_4-OCH_3(p-anisidine), $C_6H_5CH_2$-(benzyl amine), C_6H_5-(aniline). R_1=CH_3-$(CH_2)_7$-. R_2=$(CH_2)_7$-CO_2CH_3.

Fig. 4.11 Synthesis of β-amino alcohols from internal epoxy fatty acid methyl esters (methyl epoxy stearate)

different amines such as aliphatic, cyclic, and aromatic amines converted to a isomeric mixture of 1,2-amino alcohols with yields between 65 and 85% [41].

For the applications within the automotive, fuel, and electronics industries, nylon-11 also known as Rilsan(r) by the company Arkema is suitable. Nylon-11 monomers can be obtained from renewable feedstock such as castor oil or canola oil, and it can be synthesised by condensation polymerisation of the amino acid monomer 11-aminoundecanoic acid. Ricinoleic acid is obtained from pyrolised castor oil. Out of this compound in a four-step sequence, 11-aminoundecanoic acid monomer is synthesised (see Fig. 4.12).

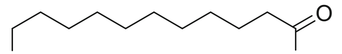

11-aminoudecanoic acid monomer

Fig. 4.12 Structure of methyl 11-aminoundecanoate, a valuable nylon-11 precursor

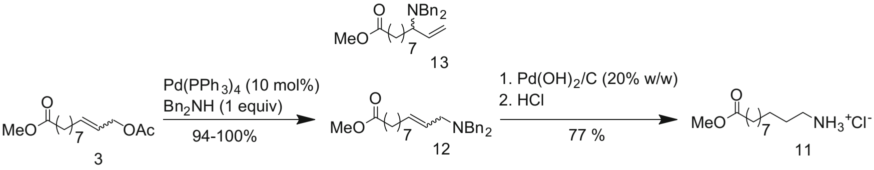


Fig. 4.13 Palladium-catalysed amination to linear saturated amino ester salts

An alternative route is the synthesis of nylon-11 monomer from canola oil. Spiccia and co-workers describe the three-step multicatalytic sequence from the methyl-undec-9-enoate to the methyl-11-aminoundecanoate hydrochloride through selective functionalisation of the unsaturated esters via sequence of ruthenium-catalysed cross-metathesis and palladium-catalysed amination and hydrogenation–hydrogenolysis steps.

Quantitative yields of the desired linear amino ester **12** adduct were obtained by palladium-catalysed ($Pd(PPh_3)_4$) addition of one molar equivalent of dibenzylamin (see Fig. 4.13). Hydrogenation and hydrogenolysis lead to the saturated primary amino ester salt. This was achieved with the heterogeneous Pearlman's catalyst ($Pd(OH)_2/C$ (20% w/w) [42].

Renewable AB-type polymers for the preparation of polyamides can also be synthesised from unsaturated fatty acid esters by Wacker oxidation followed by a reductive amination. Although in this synthesis heterogeneous catalysts are used, it shows as an example for the reductive animation from fatty acid esters. Winkler and co-workers investigated the oxyfunctionalisation of unsaturated fatty acid methyl esters (FAME) from renewable resources. Through the CO-catalyst-free Wacker oxidation the keto-fatty acid esters were gained. By reductive amination, the amine functionalisation could be achieved. The amine functionalised FAMEs 3 and 4 were achieved in good yields and excellent selectivity towards the primary amines. The reductive amination was carried out with an excess of ammonium chloride/ammonium acetate and with 20 wt% of the freshly prepared RANEY®-Nickel catalyst, leading to AB-type monomers for the synthesis of renewable polyamides (see Fig. 4.14) [43].

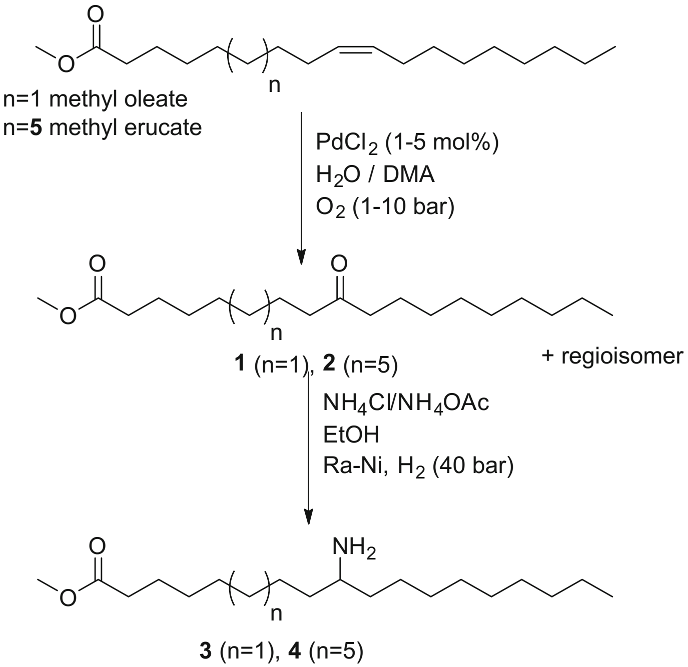


Fig. 4.14 Co-catalyst-free Wacker oxidation of unsaturated FAMEs and subsequent reductive amination to prepare amino FAMEs 3 and 4

4.2.4 Terpenes

Starting materials from renewable biomass are among others the hydrocarbon-rich terpenes (see Sect. 1.3.2). They are branched or cyclic unsaturated molecules and are gained through extraction from the leaves, flowers, and fruits of many plants and trees like conifer trees. Industrially, terpenes and other side products of the processing of trees are available through the globally acting paper industry that is eager to increase their portfolio. The structure of the terpenes consists of a distinct combination of isoprene molecules and functional groups which results in a wide variety of different substances and chemical properties.

4.2.5 Myrcene

Myrcene is a simple acyclic monoterpene without further functionalisation and is gained by pyrolysis of β-pinene. Lithium catalysed addition of amines to terpenes (conjugated double bonds) by the example of myrcene (see Fig. 4.15).

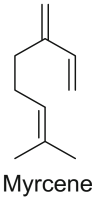


Fig. 4.15 Myrcene, an important starting material in the production of scents

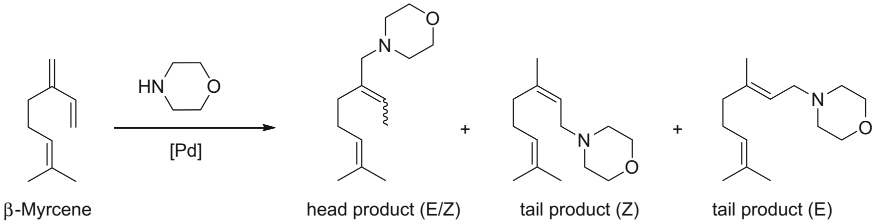


Fig. 4.16 Palladium-catalysed hydroamination of myrcene with morpholine

Myrcene is an important starting material for olefinic scents, especially for the listed production methods of menthol and top-selling alcohols nerol, geraniol and linalool in the literature. Through the direct catalysed addition of an amine to the double bond amine, derivates of myrcene can be synthesised [15]. Behr et al. reported the hydroamination of myrcene with morpholine catalysed by palladium complexes ($Pd(CF_3CO_2)_2$) with bidentate ligands like bis(diphenylphosphino)butane (DPPB) as shown in Fig. 4.16. The optimal reaction conditions for conversion and selectivity are a catalyst concentration of 0.2 mol% of the substrate, a Pd/P ratio of 1:8, toluene as the solvent, a reaction temperature of 100 °C, and a reaction time of 4 h. In this manner, a yield for the hydroamination product of up to 92% was possible. The homogenous catalyst was recycled with the applied TMS (see Chap. 3) method. ACN/heptane fulfilled the criteria of the separation concept. Besides that, the leaching of the catalyst in the extract phase was negligible low, the high catalyst activity was maintained, and good extraction properties towards the product were achieved [17]. A recycling of this system was also descripted and can be found in Chap. 10.

4.2.6 Citronellal

Another monoterpenoid is citronellal (3, 7-dimethyloct-6-en-1-al). This aldehyde can be gathered from natural resources and is best known as flavouring agent and insect repellent. Behr and co-workers describe the reductive amination of the natural product citronellal with ammonia to yield primary amine derivatives [44]. The

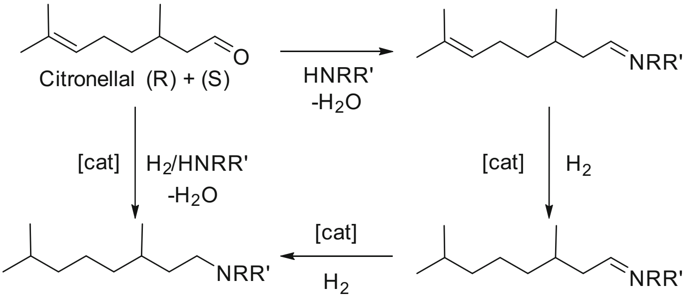


Fig. 4.17 Reaction scheme of the reductive amination of citronellal

reductive amination is a tandem reaction consisting of the two reaction steps, condensation and hydrogenation. In general as starting material for the reductive amination, ketones, aldehydes, and even alcohols can be applied. The aldimine is gained through the condensation reaction of the two substrates followed by the hydrogenation step resulting in the desired primary product amine as can be seen in Fig. 4.17.

The earlier mentioned challenge in using ammonia in amination reaction in the synthesis of primary amines is the formation of secondary and ternary side products. To control the reaction sequence, Behr et al. applied different rhodium and iridium catalysts in addition to the three phosphorus ligands TPPTS, BISBI, and BINAS as seen in Fig. 4.18. Yields of 78% amine and enamine were achieved with the rhodium complex formed from the precursor $[Rh(cod)Cl]_2$ and coordinated TPPTS molecules. The reaction was performed in a biphasic liquid–liquid system consisting of an aqueous phase and an organic phase. While the former contains the catalyst, the water soluble ligands, and ammonia, the latter carries the myrcene and products. The separation of catalyst and products successfully suppressed the catalyst leaching during the reaction and therefore fortifies the industrial relevance of the concept. By addition of the surfactant cetyl trimethylammonium chloride (CTAC), the yield of primary amines and enamines could be raised to 87%. The optimal results were

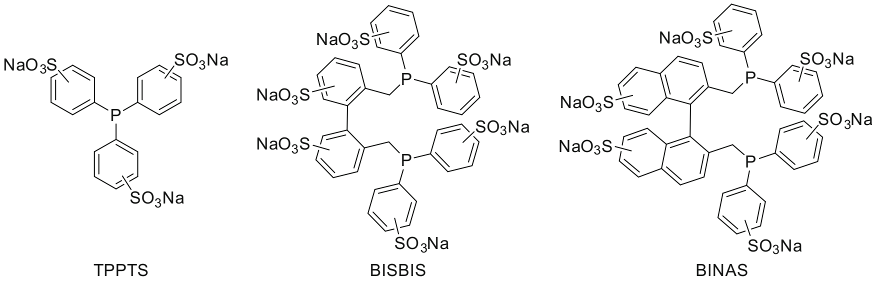


Fig. 4.18 Phosphorus ligands investigated in the reductive amination of citronellal (Behr et al. [44])

obtained at 130 °C, 60 bar of hydrogen pressure, 0.5 mol% $[Rh(cod)Cl]_2$, 2 mol% TPPTS, and 0.5 mol% CTAC related to the amount of substrate. As organic solvent toluene was used, the reaction was performed for 6 h [44].

4.3 Conclusion

The amination of renewable feedstocks is still a field with a lot of potential for scientific works. Nevertheless, some promising applications for the productions of building blocks have already been investigated with success. Regarding the huge market available for nitrogen-containing chemicals such as polymers or pharmaceuticals, the homogenously transition metal catalysed amination is versatile tool that can be used for synthesis at mild reaction conditions under high atom economy. The authors therefore recommend interested groups to participate in the pioneering to clear the way for large scale amination of renewable feedstocks for a more efficient chemical industry.

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Chapter 5
Telomerisation of Renewables

T.A. Faßbach, Arno Behr and Andreas J. Vorholt

5.1 Introduction

In homogeneous catalysis, the term *telomerisation* refers to the dimerisation of 1,3–dienes including an addition of a H–acidic nucleophile [1]. The most popular and investigated example is the telomerisation of 1,3–butadiene with methanol yielding 2,7–octadienyl methyl ether (*E*/*Z*) and—in minor amounts—3–methoxy–1,7–octadiene (Fig. 5.1).

The telomerisation reaction was primarily described by Smutny in a patent for *Shell Oil Company* in 1966 [2]. He discovered the reaction while investigating the dimerisation of 1,3–butadiene with homogeneous palladium catalysts.

The mechanism was postulated by Jolly [3] and is drawn in Fig. 5.2. A (σ)-palladium complex with a phosphine ligand is the resting state of the mechanism. After dissociation of a ligand, two dienes coordinate to the metal centre. In the first step (A), a C–C bond is formed and a C_8-chain with a η^1- and a η^3-bond to the palladium centre is build. In the next step (B), a nucleophile coordinates to a metal centre. The hydrogen migrates in step C into η^1-bond. The addition of the nucleophile adds to the η^3-bond (D).

Aside from a few other transition metals such as rhodium [4, 5] or nickel and platinum [6], palladium is still the most widely used catalyst due to its high activity. There are many examples for different nucleophiles that are active in this reaction, yet alcohols and amines are the most common ones [7].

Despite the fact that the telomerisation is an atom-efficient catalytic reaction, usually occurring at high reaction rates, to this date there are only two industrial applications. The process run by *Dow Chemicals* employs the above-mentioned telomerisation of 1,3–butadiene with methanol. The obtained methyl octadienyl ether is hydrogenated to the saturated methyl octyl ether, which is cleaved finally to form 1–octene for polymer purposes in very high purities. Along with the 1–octene, methanol is formed, which can be employed again in the telomerisation of 1,3–butadiene (Fig. 5.3) [8].

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Catalysis by Metal Complexes 39, DOI 10.1007/978-3-319-54161-7_5

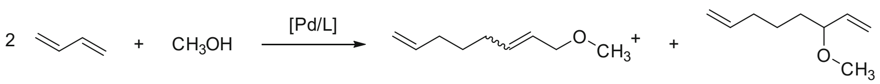

Fig. 5.1 Telomerisation of 1,3–butadiene with methanol

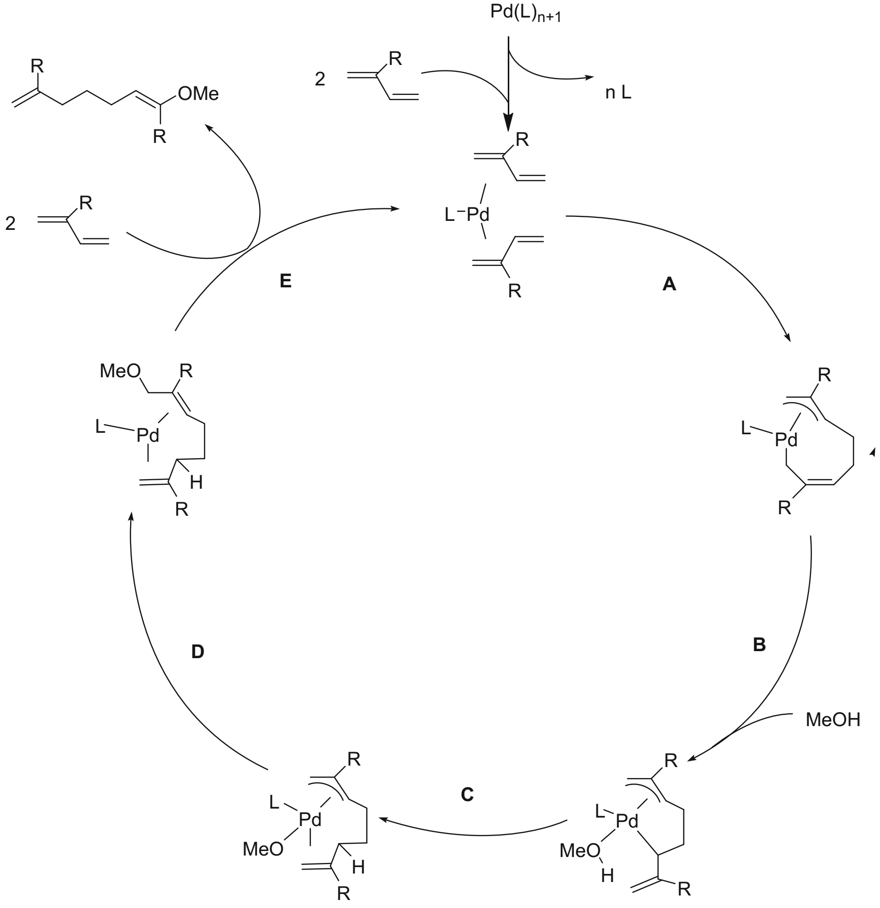

Fig. 5.2 Telomerisation mechanism

The second commercial process, carried out by *Kuraray*, is using the telomerisation of 1,3–butadiene with water to form 1–octanol (Fig. 5.4) [9].

The reaction is carried out in a solvent mixture of water and sulfolane using a water-soluble TPPMS (=triphenylphosphine-monosulfonate) ligand. The product is subsequently extracted using hexane; the catalyst—immobilised in the aqueous phase—is recycled to the reactor.

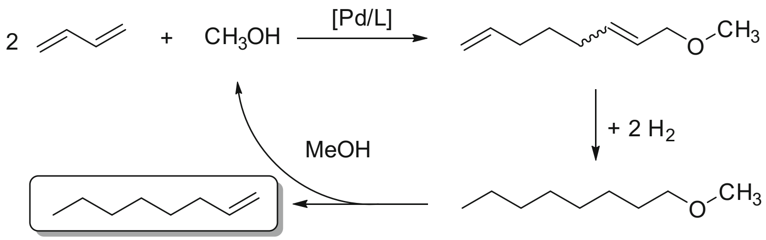

Fig. 5.3 Production of 1–octene starting from 1,3–butadiene and methanol

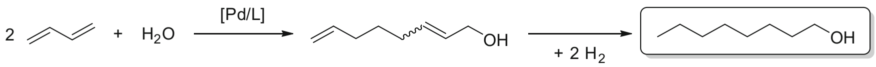

Fig. 5.4 Production of 1-octanol from 1,3–butadiene and water

5.2 Telomerisation Using Renewable Dienes

Although the telomerisation is a widely investigated reaction with industrial applications, till now only a few dienes have been used successfully. Aside from very few others, mainly 1,3–butadiene and isoprene are mentioned in the literature. Both are gained through petrochemical processes [10, 11].

To this date, there is only one example for a homogeneous telomerisation, applying a diene based on a renewable feedstock. Behr and Vorholt realised the telomerisation of *β*–myrcene with diethylamine using a thermomorphic multi-component solvent systems for catalyst recycling (Fig. 5.5) [12].

Due to the asymmetric substitution of the 1,3–diene chain of myrcene, there are several possible ways to build up the 2,7-octadienyl chain and to attach the nucleophile to this backbone. Regarding all possible combinations of linkage, there are 12 different isomers of the pictured (linear *head-to-head-*(*E*)) product. After the reaction, the thermomorphic solvent system consisting of acetonitrile and heptane was able to separate the palladium catalyst very effectively from the product fraction.

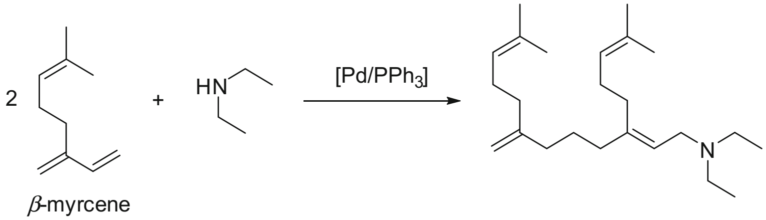

Fig. 5.5 Telomerisation of *β*-myrcene with diethylamine

Lately, the group of Bogel-Lukasik discovered the heterogeneous palladium-catalysed telomerisation of β–myrcene with glycerol in supercritical CO_2 [13].

5.3 Telomerisation Using Renewable Nucleophiles

There are several examples for telomerisations with nucleophiles based on a renewable feedstock. In contrast to the dienes, the "green" potential of the nucleophilic component was comparatively early investigated.

5.3.1 Lignin-Derived Phenols

Phenol was one of the first nucleophiles used in the telomerisation [14]. Over the years, several investigations have been carried out, regarding halogenated phenols and different catalysts. For instance, Beller achieved a shift towards the side reaction of *C*-allylation in contrast to the telomerisation, yielding *O*-allylated products (Fig. 5.6) [15]. When a low ligand excess (up to 3:1) of PPh_3 is maintained and especially in the presence of bases, like trimethylamine, the selectivity towards the *C*-allylated product reaches up to 92%.

In general, phenol is synthesised out of benzene in the Hock process [16], but lately, much effort has been made to realise the usage of lignin-derived phenols.

In order to develop a reaction system that enables the valorisation of lignin-derived phenols, Weckhuysen et al. investigated the reactivity of methyl- and methoxy-substituted phenols, respectively (Fig. 5.7) [17].

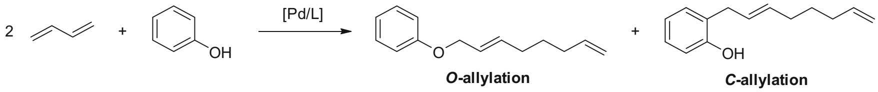

Fig. 5.6 Telomerisation of phenol leads to *O*- and *C*-allylated products

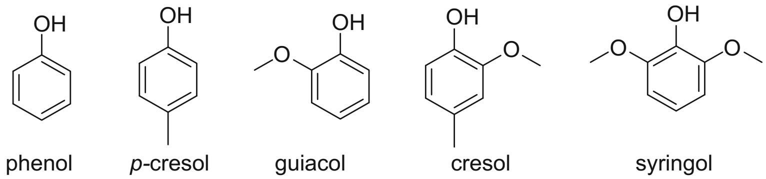

Fig. 5.7 Lignin-derived phenols

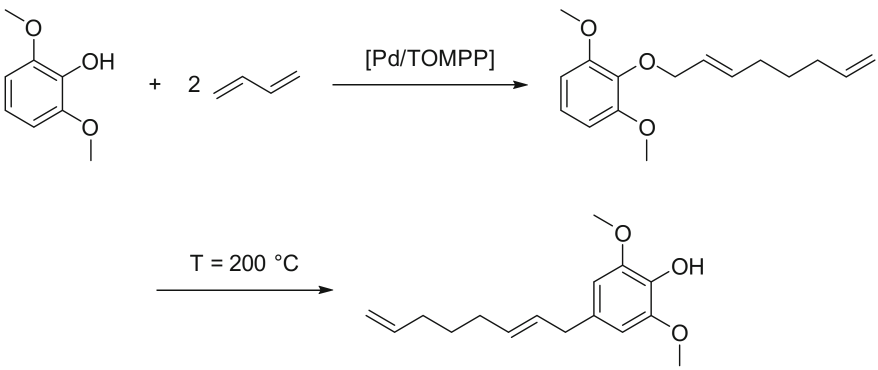

Fig. 5.8 Telomerisation of syringol with 1,3–butadiene followed by a Claisen rearrangement

The group used a Pd/TOMPP (TOMPP = tris(2-methoxyphenyl)phosphine) catalytic system, which they had established earlier for the telomerisation of 1,3–butadiene with glycerol [18]. These nucleophiles were successfully telomerised with significantly different yields. Phenol and *p*–cresol gave only poor yields of the desired products. In contrast to this, the substrates with electron-donating groups in *ortho*-position (guaiacol, cresol, and syringol) are much more likely to react. With a fourfold excess of 1,3–butadiene conversions of the nucleophiles, over 90% were achieved at a reaction temperature of 60 °C.

Gaining a wide field of applications for these products, the group also investigated a subsequent Claisen rearrangement (Fig. 5.8).

5.3.2 *Renewable Polyols*

When polyvalent alcohols are employed, the problem of regioselectivity arises. Starting from a polyol, like glycerol the telomerisation of 1,3–butadiene leads to several products with different substitution grades (Fig. 5.9).

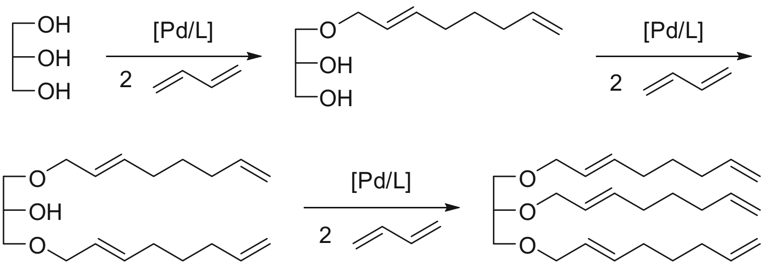

Fig. 5.9 Mono-, di-, and tritelomer of glycerol

Often, a selective pathway to monotelomers is desired because these are surfactant precursors. On the one hand, it is very difficult to influence the reaction system to yield mainly mono-substituted polyols; on the other hand, they are promising building blocks for industrial chemicals, e.g. surfactants. Additionally, biomass-derived diols can be converted to their respective ethers [19–21].

One approach to achieve high selectivity towards monotelomers derived from nucleophiles bearing multiple hydroxyl groups is liquid–liquid two-phase systems. On an industrial scale, aqueous biphasic systems are used for catalyst separation only. In these cases, the catalyst is dissolved in the aqueous (polar) phase, while the substrates and products are present in the organic (non-polar) phase. After the reaction, the products and the catalyst can be separated easily. In the case of the telomerisation of polyvalent nucleophiles, this concept offers another advantage. The significantly lower solubility of octadienyl-substituted substrate in the polar phase separates it physically from the catalyst, which lowers the probability of a subsequent reaction. This concept was applied to the telomerisation reaction at first by Driessen-Hölscher [22]. The telomerisation of 1,3–butadiene with ammonia could be realised with Pd/TPPTS catalyst yielding primary amines almost exclusively, where the classical Pd/PPh_3 catalyst leads mainly to secondary amines (Fig. 5.10).

5.3.2.1 Glycerol

The research concerning the telomerisation with glycerol focuses mainly on the mono-substituted product as this is a promising building block for surfactants and detergents [23]. Setting up a telomerisation between polyvalent alcohols and 1,3–dienes implies difficulties due to the poor miscibility between those two compounds. In 2003, Behr reported the selective monotelomerisation of glycerol and some short-chain diols [24].

These systems are based on the concept of a water-soluble catalyst [e.g. consisting of Pd/TPPTS (TPPTS = triphenylphosphinetrisulfonate)] and a water-soluble nucleophile. Only minimal amount of the non-polar 1,3–diene is dissolved in water. The reaction takes place and the alkylated product is no longer soluble in the catalyst phase. Along with the advantage of a high selectivity comes the possibility of

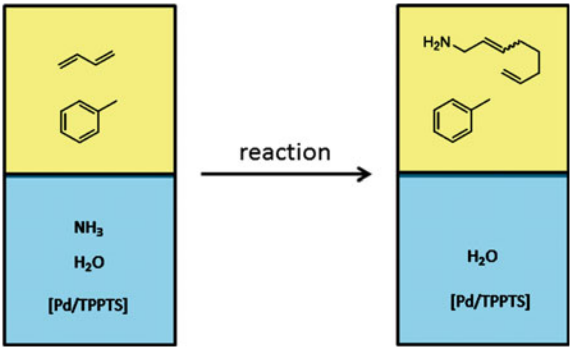

Fig. 5.10 Telomerisation of 1,3-butadiene with ammonia in a liquid–liquid biphasic system

a catalyst recycling. *Behr* and *Urschey* could recycle the catalyst for the glycerol telomerisation for at least five times. Later, Behr and Leschinski managed to scale this reaction up to a miniplant scale with closed recycling streams of glycerol and 1,3–butadiene (see Sect. 8.1) [25, 26].

In 2010, the telomerisation of 1,3–butadiene with glycerol in aqueous biphasic systems was studied in-depth, by Castanet et al. The main focus in these investigations was on the influence of reaction parameters such as temperature, amount of water and base or different sulfonated phosphine ligands [27]. Varying these parameters, they managed to control the product distribution towards mono- and di-telomerisation products, respectively.

Another approach towards the etherification of glycerol via telomerisation was made by the group of Weckhuysen. They used tris(*ortho*-methoxyphenyl)phosphine (TOMPP) ligands and $Pd(acac)_2$ as a precursor and could run the reaction without any solvent [18, 28–30]. High yields were obtained (over 90% glycerol ethers), but high selectivities towards one of the alkylated glycerol derivatives could not be reported.

The first example for a telomerisation of isoprene and glycerol is given by Rothenberg et al. in 2009 [31]. A solvent mixture of dioxane and PEG-200 was applied and a Pd/carbene catalytic system led to a mixture of PEG- and glycerol-telomers alongside with significant yields of the dimerisation product. Interestingly, only monotelomers of glycerol were yielded.

5.3.2.2 Sugars and Sugar-Derived Polyols

The first telomerisation with an unmodified natural carbohydrate was reported by Hill et al. in 1994 [32]. A simple catalyst system, consisting of $Pd(acac)_2$ and PPh_3 in a solvent mixture of water and isopropanol (20:80 by weight) leads to sucrose octadienyl ethers with yields up to 63%. In 1997, the already mentioned concept of aqueous biphasic systems was adapted to the telomerisation of 1,3–butadiene with sucrose by Mortreux et al. [33]. Using isopropanol as a second organic phase, they could reach selectivities towards the monoether of 66% with conversions of 73%. Further investigations, concerning catalyst concentration and metal/ligand ratio, have been made by the group of Pinel [34]. They also made some progress in the modification of starch and its derivatives by aqueous telomerisation (Fig. 5.11) [35].

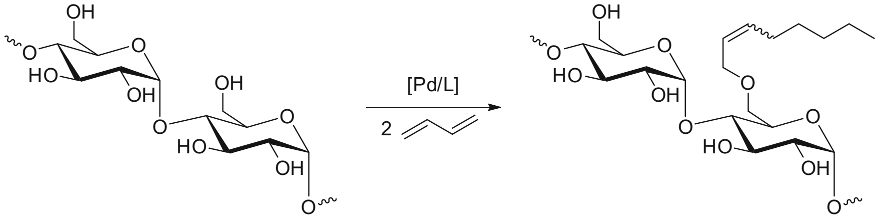

Fig. 5.11 Telomerisation of starch with 1,3-butadiene

Estrine et al. [36] and Hénin et al. [37] successfully enhanced the substrate spectrum to pentoses, such as D–xylose and L–arabinose. Using DMF as a solvent, selectivities up to 90% towards the monoether were reached with conversions of 80%. Further studies in this field were made by Bessmertnykh and Hénin in 2005 [38]. They also managed to control the selectivity towards the amount of ether linkages formed. Depending on the structure of the amine base that is used, the reaction yields either more mono- or diethers [39]. Estrine et al. [40] investigated the opportunities in heterogenising the Pd/TPPTS catalyst on an alumina support. A turnover number of 500 could be held up for five successive runs.

5.3.3 Telomerisation with CO_2

Another renewable building block, which can be employed in the telomerisation reaction, is CO_2. The very first report of the successful conversion of 1,3–butadiene with CO_2 was made by the group of Sasaki et al. in 1976 [41]. They reported the formation of C_9-lactones and their corresponding carboxylic acids in the presence of a Pd/diphos (=diphenylphosphinoethane, dppe) catalytic system (Fig. 5.12).

Unfortunately, the main product of this reaction is different dimers of 1,3–butadiene. Two years later, Musco et al. [42] found that non-chelating phosphines (like PPh_3) could yield significantly more products, if non-polar solvents, e.g. benzene, are used. Also, they used the much more basic phosphine ligand PEt_3, which led to high yields of the desired lactones. A deeper understanding of this reaction was gained by Behr et al. by systematically investigating the course of the reaction, as well as the influence of the nature of the ligand [43, 44].

Behr and Heite [45] transferred the above-mentioned reaction into a miniplant scale, using a slightly different catalytic system, consisting of $Pd(acac)_2$ and PCy_3 (see Sect. 8.1). The solvent for the reaction was acetonitrile. The miniplant was operated continuously, by recycling the volatile substrates and extracting the products from the catalyst using 1,3,4-butanetriol. The miniplant could be run for 24 h continuously, yielding comparable results to the batch experiments. Investigations considering polar solvents, like carbonates, showed that cyclic carbonates (like propylene carbonate) are leading to better results than nitriles, like acetonitrile, does [46].

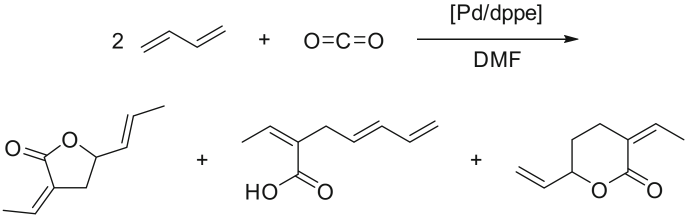

Fig. 5.12 Formation of lactones and carboxylic acids out of 1,3-butadiene and CO_2

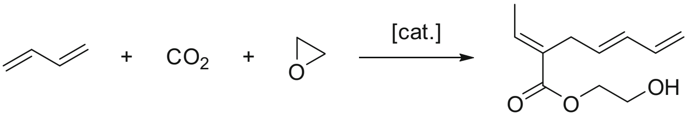

Fig. 5.13 Synthesis of hydroxyl esters from 1,3-butadiene, CO_2, and oxiranes

Interestingly, the reaction can be modified with additional compounds, e.g. oxiranes (ethylene oxide, propylene oxide), to gain their respective hydroxyl-functionalised ester (Fig. 5.13) [47].

In 2016, Sharif et al. could demonstrate that the Pd/TOMPP catalytic system, which is highly active for 1,3–butadiene and glycerol, is also capable of an effective catalysis for the telomerisation of 1,3–butadiene and carbon dioxide as well [48].

Lately, much effort has been put into the subsequent conversion of the yielded lactones in polymerisation reactions. It could be shown that a radical polymerisation of these lactones is possible [49, 50].

Overall, it can be stated that the telomerisation of 1,3–dienes with carbon dioxide is an elegant and effective use of this renewable building block to gain valuable products [51–54].

5.4 Conclusion

Telomerisation is a special multicomponent reaction which features the dimerisation of dienes and nucleophiles. The versatile combination of different of these substrates gives an atom economic way to use the resulting molecules as, e.g., surfactants or monomers. Renewable dienes such as myrcene can be applied in the telomerisation to yield selectively C_{20} groups. Nucleophiles such as glycerol or sugar derivatives can be incorporated easily in this synthesis pattern. Therefore, telomerisation is a useful tool to convert renewables into valuable products for several applications.

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Chapter 6
Oxidation of Renewables

Sabrina Baader and Melanie Kim Müller

6.1 Introduction

Oxygen, one of the most essential elements in nature, plays a key role in chemistry since many chemical structures get their defined functionality through the presence of *O*-heteroatoms; examples include alcohols, ethers, carbonyl compounds, and most importantly epoxides. From a global perspective, C–O bonds formed via oxidation reactions belong to the most applied transformations in the production of pharmaceuticals up to large-scale commodities from petroleum-based feedstocks. Around 600 Mio tons of various chemicals are annually produced via oxidations leading to one-third of the most valuable organic products and intermediates such as terephtalic acid, ethylene oxide, and formaldehyde [1].

Presently, heterogeneous as well as homogeneous systems operate on large scales, with various oxidants such as oxygen either in pure form or as part of the air, hydrogen peroxide, hydroperoxides, or peroxy acids [2]. Examples of advantageous commercial processes include the production of ethylene oxide from ethylene with molecular oxygen catalysed by silver salts [3], the preparation of terephthalic acid from p-Xylene using molecular oxygen in the presence of manganese and cobalt salts (Amoco process) [4], and the Wacker oxidation of alkenes to carbonyl compounds catalysed by palladium and copper chlorides [5].

While oxidation reactions are considered as one of the most important processes in modern chemistry, they also belong to the most problematic chemical transformations [6]. Commercial methods, particularly oxidations leading to fine chemicals, call for oxidants which release the formal oxygen equivalent using stoichiometric quantities of toxic inorganic reagents such as permanganate and dichromate and large amounts of inorganic salts. Thus, such oxidants bear a high ratio of the mass of waste per mass of product, the so-called E-factor (Table 6.1).

To meet the restrictions of sustainable chemistry, the overall synthesis of oxidised products must be accomplished with a low E-factor under clean and safe conditions [7]. In order to develop "greener" oxidation reactions that have little or

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Table 6.1 Traditional oxidants and their E-factors

Oxidant	Oxygen generation reaction (mol O_2/mol oxidant)	E-factor
Potassium bichromate	$K_2Cr_2O_7 + 4\ H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4\ H_2O + \mathbf{1.5\ O_2}$	13.3
Sodium hypochlorite	$NaOCl \rightarrow NaCl + \mathbf{0.5\ O_2}$	3.65
Chromic acid	$2\ CrO_3 \rightarrow Cr_2O_3 + \mathbf{1.5\ O_2}$	3.17
Hydrogen peroxide	$H_2O_2 \rightarrow H_2O + \mathbf{0.5\ O_2}$	1.13
Ozone	$O_3 \rightarrow \mathbf{1.5\ O_2}$	0

E-factor = mass waste/mass oxygen

no pollution potential or environmental risk, molecular oxygen is considered as the ideal reagent. In particular for the activation of O_2 and its selective introduction into molecules, the use of metal complexes is mandatory [8]. Moreover, often only one of the two oxygen atoms is transferred to the substrate to give the oxidised molecule. To avoid extra amounts of reducing agents, methods using both oxygen atoms are currently under investigation. Regarding the general improvement of oxidation chemistry, research does not only focus on petrochemical-based processes and the improvement of the oxidants, but also involves the incorporation of renewable starting materials.

Oxidations of renewables represent an interesting strategy for the production of bulk and fine chemicals due to the brought applicability of the products in functionalisation. Many renewables, e.g. vegetable oils or terpenes, appear in a reduced form containing a double bond. Depending on the starting material, catalyst, and oxidant, different products such as epoxides, alcohols, aldehydes, or ketones become easily available from unsaturated natural products. Furthermore, oxidative cleavage of internal double bonds plays an important role among oxidation reactions since it allows the formation of aldehydes, esters, diols, and dicarboxylic acids altering the chain length at the same time [9, 10].

In contrast to polysaccharide- or lignin-derived platform molecules, terpenes as well as vegetable fats and oils have relatively high carbon content, and therefore, conversion routes of these substrates often involve reactions to increase the oxygen content. Both unsaturated natural terpenes and fatty acids and their derivatives can be oxidised in numerous ways providing access to important valuable chemical feedstocks as demonstrated in Fig. 6.1.

The following chapters cover industrially relevant oxidative upgrade processes of renewable substrates while focusing on sustainable aspects of the comprehensive approaches including quality of oxidants, safety aspects of the methods, availability of the starting materials, and product applications.

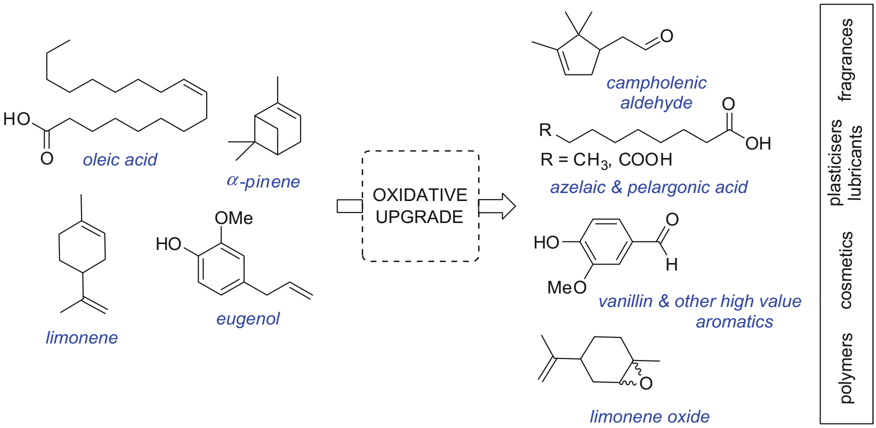

Fig. 6.1 Overview of important platform chemicals from renewable resources and their industrial applications

6.2 Fatty Acids and Fatty Acid Derivatives

Oxidation products from natural oils and fats are routinely applied in industry, particularly in the polymer field. With assistance of oxidation reactants [OX] such as hydrogen peroxide, hydroperoxides, or peracids, unsaturated fatty compounds, either the natural unsaturated vegetable oils or the corresponding free fatty acid and esters, are modified at the olefinic chain [11]. Possible products are epoxides and vicinal diols which form in the presence of hydrogen peroxide, mono- and dicarboxylic acids, as well as aldehydes obtained via cleavage of their C=C bonds (Fig. 6.2). Radical oxidation at the allylic position of fatty derivatives leads to aldehydes and alcohols while Wacker-type oxidations deliver keto fatty acids [12].

To date, the only commercial source of epoxidised oils is based on the Prileshajev peracid process which lacks of selectivity towards the desired epoxides and harsh reaction conditions, e.g. high concentration of hydrogen peroxide and strong acids [13, 14]. Furthermore, several methods for the epoxidation of unsaturated fatty compounds have been reported including the epoxidation with aldehydes, molecular oxygen, dioxiranes, as well as with high valence catalysts based

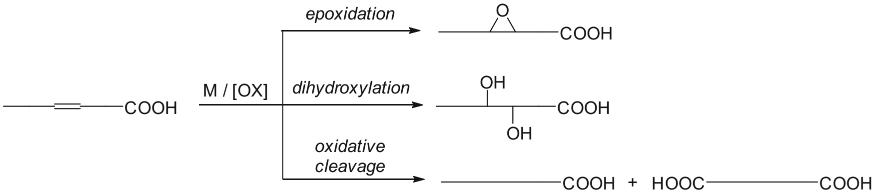

Fig. 6.2 Selected oxidation reactions of unsaturated fatty acids

on H_2O_2/tungsten heteropolyacids, H_2O_2/methyl trioxorhenium, and enzymatic methods [15–18]. A good epoxidation procedure for the conversion of oleic acid into 9,10-epoxysteraic acid in 87% selectivity was developed by Ziólkowski using organic hydroperoxides in the presence of a molybdenum catalyst [19]. Typical homogenous catalyst for the epoxidation of fats and oils with H_2O_2 includes Mo$(CO)_6$ or $Mo(O)_2(acac)_2$ [20]. Epoxy oils and fats can be used as PVC plasticisers, flame retardants, heat stabilisers, additives in lubricants and cosmetics, and many others [21]. Subsequent cleavage of the epoxide structure leads to vicinal diols. A more elegant approach towards diol formation involves the direct dihydroxylation of unsaturated fatty compounds with hydrogen peroxide. For this purpose, tungstic acid (H_2WO_4) or rhenium complexes such as methyltrioxorhenium (CH_3ReO_3) are used as catalysts which need to be active under mild reaction conditions (25–50 °C) as shown by Herrmann [22]. Dihydroxylated fatty acids are important materials in chemical, food, and cosmetic industry, as well as crucial signalling compounds related to human disease [23].

In comparison with fatty acid-based diols, products obtained via oxidative cleavage of unsaturated fatty acid derivatives, such as C9-chain carboxylic acids, represent even more important platform chemicals and therefore find wide industrial application [24]. Azelaic acid (nonane diacid, AA), obtained from oleic acid or its methylester, is the main component for the production of nylon-6,9 used for fibres and resins produced in high volumes of several 1000 tons/year [25]. These oleochemically derived dicarboxylic acids can simplify the condensation of the polymers due to their unique properties, such as high impact strength, hydrolytic stability, hydrophobicity, lower glass transition temperatures, and flexibility [26, 27]. Furthermore, dicarboxylic acids esters are used as lubricants and hydraulic fluids over a wide temperature range [28], as well as plasticisers for polyvinyl chloride [29]. Pelargonic acid (nonanoic acid, PA) is also applied in the manufacture of cosmetics, lubricants, and plasticisers [30]. Aldehydes obtained from reductive ozonolysis such as nonanal and other C8–C13 straight chain fatty aldehydes are important aroma active compounds used in the perfume industry [30] while 9-oxononanoic acid represents a precursor for biopolymers (Fig. 6.3).

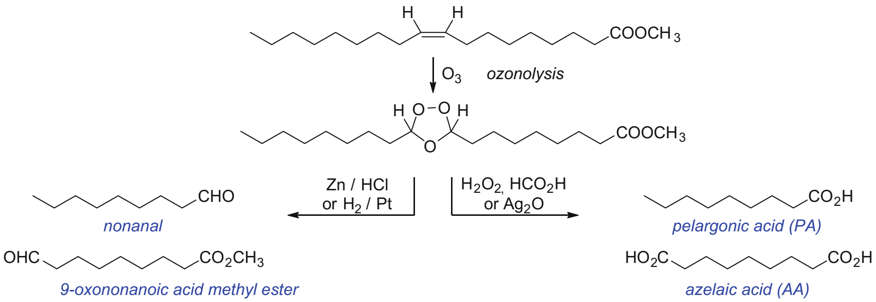

Fig. 6.3 Traditional preparative double bond cleavage reactions of oleic acid methyl ester via reductive (*left*) and oxidative ozonolysis (*right*) [31]

Traditional methods for the oxidative double bond cleavage of fatty compounds as shown in Fig. 6.3 include reductive or oxidative ozonolysis. The in situ formed ozonide is selectively converted into the C9-cleaved products without the formation of environmentally harmful side products. However, using ozone on large scale is expensive and requires powerful cooling system for explosion protection. To date, the oxidative cleavage of oleic acid via ozonolysis is the only commercialised process by Emery Oleochemicals [32]. Beside ozonolysis, oxidative cleavage of plant oils has been reported with catalysts and stoichiometric amounts of harsh reagents such as nitric acid [33], sodium hypochloride [34, 35], periodate [36], as well as peracetic acid [37]. In order to find a sustainable alternative to the hazardous methods to produce azelaic and perlargonic acid, new transition metal catalysed methods were developed. The catalytic activity of transition metals allows using more benign oxidants [38].

Considering the mechanism of oxidative cleavage of unsaturated fatty acids, its seems more complicated to cleave these functionalised molecules compared to simple or even cyclic alkenes, due to the presence of the carboxylic group causing side reactions and inhibiting radical reaction pathways. Catalytic systems based on transition metal tetroxides can either undergo vic-diol formation in case, e.g. by tungsten (H_2WO_4/H_2O_2) or osmium, while in situ formed RuO_4 complexes directly cleave the organic tetroxide intermediate (Fig. 6.4). In contrast, the formation of an epoxide followed by hydrolysis to diols was mainly described for, e.g., molybdenum [37].

In general, molecular oxygen is considered as the ideal oxidant. However, oxidations with molecular oxygen are somewhat difficult to control and less selective in comparison with other oxidants. Thus, the aerobic catalytic cleavage of oleic acid or methyl oleate is rarely described in the literature. Early reports in this

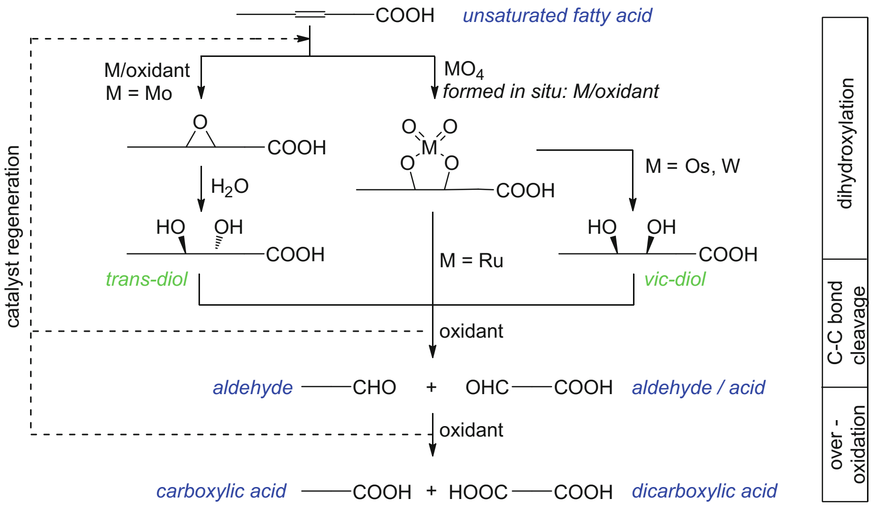

Fig. 6.4 Different reaction pathways for one and two step oxidative cleavage procedure of unsaturated fatty acids with and third-row transition second-metals [39]

field are based on cobalt (Co oleate or naphthenate) [40] or vanadium (VO_4^{3-}/V_2O_5, 400–500 °C) [41] which lack of reactivity and selectivity towards the desired cleaved products (<45% AA after 72 h). Dapurkar et al. used more active recyclable microporous and mesoporous chromium-, manganese-, and cobalt-coated catalysts in the aerobic double bond cleavage of oleic acid in supercritical CO_2 which afforded 32% of the C_9-chain (AA and PA) acids after 8 h [42]. The first breakthrough in oleic acid cleavage regarding high selectivity (yields >90% of AA and PA) was achieved by Kawamoto and Yoshioka in 1982 using RuO_2 as the catalyst [43, 44]. However, the greatest drawback of this procedure presents the addition of stoichiometric amounts of aldehydes as sacrificial reagents. In continuative research work, Köckritz et al. utilised an osmium catalyst (OsO_4/K_2OsO_4) also in combination with an aldehyde as co-oxidant [45]. The formation of the corresponding waste products does not go along with the requirement of green chemistry.

The oxidative cleavage with molecular oxygen or air did not yet deliver the requested selectivities with respect to azelaic and pelargonic acid, since the radical autoxidation as competitive reaction largely depletes the desired products.

According to the limited selectivity of the oxidation of carbon double bonds with O_2, different one- and two-step processes were examined for the oxidative cleavage of unsaturated fatty acids with H_2O_2. Apart from oxygen, hydrogen peroxide is the cheapest and also most environmentally friendly oxidant which results in water as the only side product [25]. Industrially, H_2O_2 is produced by oxygen reduction in the anthraquinone process developed by BASF [46].

In 1993, first research work regarding the direct oxidative C–C double bond cleavage of oleic acid with H_2O_2 was carried out by Katsura who used in situ generated tetrakis-(oxodiperoxo-wolfram)-phosphat in combination with a phase transfer catalyst. In a two-phase system, they reported yields of around 90% of the desired carboxylic acids [47] which led to further optimisation [48–52]. Already one year later, Johnstone et al. published a promising catalyst system based on MoO_3/$RuCl_3$/Didecyldimethylammuniumbromid in tert-butanol which yielded 100% AA und 43% PA. After 4 h, the starting material was fully converted, but a large excess of H_2O_2 (7–8 equiv.) is required which tends to decompose at the Ru catalysts [53]. A molybdenum-based peroxo complex $MoO(O_2)[C_5H_3N(CO_2)_2](H_2O)$ investigated by Turnwald yielded 82% AA along with equal yields of nonanal after 24 h at 90 °C [52]. Using a heterogeneous tungsten oxide catalyst supported on silica, Noureddini and Kanabur achieved only moderate yields of azelaic acid while the conversion was 86%. Similar yields but lower conversion after 1 h at 130 °C was demonstrated for unsupported tungsten oxid [54]. In 2013, Behr et al. showed that $Ru(acac)_3$/dipicolinic acid is suitable for the cleavage oleic acid and methyl oleate [55]. In contrast to oleic acid which delivered around 60% of the cleaved C9–chain acids, better yields of 81% of azelaic acid methyl ester and 86% of pelargonic acid were obtained after 24 h when using methyl oleate as starting material. Multistep procedures for the production of mono- and dicarboxylic acids include ether epoxidation or dihydroxyliation as pointed out in Fig. 6.4. In 1999, Oakley et al. developed a tungsten-based two-step procedure in which the dihydroxylated intermediates were cleaved by the addition of a cobalt catalyst (Co(acac)$_3$/N-hydroxyphathalimide) in the presence of oxygen giving a maximum yield of 20% azelaic and perlargonic acid [56]. Since the dihydroxylation of fatty acids was already investigated in much more detail using Re [22, 57], Mo, and W catalysts [34], the studies of Santacesaria et al. due to a deeper understanding of the second reaction step, did dramatically improve the yields of the desired products (56%) [58, 59]. Even better results were obtained with the conditions found by Warwel and Rüsch who used Re_2O_7/H_2O_2 in the DSME (9,10-dihydroxy-stearic methyl ester)-cleavage achieving yields of 78% [34, 37]. More recently in 2009, Fujuitani published the aerobe DSA (9,10-dihydroxy-stearic acid)-cleavage in the presence of Co, Mn, and Co-Mn-Br catalysts which afforded around 90% yields of the desired mono- and dicarboxylic acids [60].

In 2012, the investigation of the catalytic oxidation of methyl oleate showed that the catalyst system $RuCl_3$/dipicolinic acid, which was already described as a convenient catalyst for the epoxidation of alkenes by Beller and co-workers [61], is also a suitable catalyst for the selective epoxidation of methyl oleate [62]. The epoxide was obtained with high yield amounting to 88%. Further investigations showed that $RuCl_3$ as well as the catalyst $RuCl_3$/dipicolinic acid can also cleave the vicinal diol into the carboxylic acids AA and PA, however, at varied reactions conditions [55]. The systematic optimisation of the reaction led to the formation of azelaic acid monomethyl ester in high yields amounting up to 86%. The catalytic cleavage of the diol with oxygen using a catalyst system of Co(acac)$_3$ and N-hydroxyphthalimide is also feasible [63]. This reaction was carried out in a small loop-type reactor which enabled very safe oxidation conditions. The carboxylic acids azelaic acid monomethyl ester and pelargonic acid could be synthesized in yields of about 65% each. Recently, vicinal dihydroxy derivatives of oleic acid, methyl oleate, and erucic acid were converted by oxidative cleavage to di- and monocarboxylic acids, respectively, in the presence of highly dispersed gold particles (Au supported on Al_2O_3) by Köckritz et al. [64]. Although high yields of 86% azelaic acid and 99% pelargonic acid were obtained in 260 min at 80 °C starting from 9,10-dihydroxystearic acid, the main drawback of this system was the significant decrease in the catalytic activity after catalyst recovery.

For further information on oxidative cleavage with homogeneous as well as heterogeneous transition metal systems, see reviews by Spannring [38] and Do [39]. Another possible two-step pathway, which is not discussed in this chapter in detail, is based on metathesis and excludes a direct oxidation of the internal double bonds. Thus, the unsaturated fatty compounds are first cleaved by ethenolysis followed by oxidation of the terminal double bonds [25]. Beside transition metal-based oxidative cleavage reaction, enzymatic methods are known to be mild and very selective, as reviewed by Rajagopalan et al. [65].

With the featured single- and multistep processes for the oxidative cleavage of fatty acids, mono- and dicarboxylic acids can be obtained in remarkable yields. Homogeneous catalysts based on transition metals such as osmium, cobalt, molybdenum, chrome, gold, manganese, iron, ruthenium, and tungsten are applied, although the lack of catalyst recovery is always an obstacle for large-scale implementation.

Heterogeneous catalysts have better recycling possibilities, but a lower conversion, due to low active site availability or pore diffusion limitations. Lots of efforts are ongoing to develop methods with more than 90% conversion, solving the lack of recycling ability, avoiding metal contamination and toxic waste, as well as improving the selectivities to finally meet the restrictions of green chemistry.

6.3 Terpenes and Terpene Alcohols

Terpenes are hydrocarbons, usually possessing a strong odour, which derive biosynthetically from units of isoprene and are produced by a great variety of plants. Many terpenes autoxidise when they are exposed to air. Among that huge group of secondary metabolites that occur in essential oils and are used as fragrance compounds, there are several examples where the autoxidation is an undesired issue because of allergenic properties of the oxidised products [66]. But on the other hand, directed oxidation of this sufficiently abundant hydrocarbon class, for example in the allylic position, provides functionalised molecules that are important fine chemicals or intermediates [67]. Early work on the oxidation of terpenes using molecular oxygen was already conducted by Reese et al. in 1950 [68]. Ten years later, Bernhard et al. investigated the mechanism of the autoxidation of (+)-limonene [69], which is by far the most industrially relevant monocyclic monoterpene. (+)-Limonene is the major constituent of citrus peel oils and is obtained as a side product from orange juice production. Besides the use as a fragrance, one major limonene-based product is the ketone carvone [70], which can be obtained, e.g., via Wacker-type oxidation (Fig. 6.5). Carvone itself is an excellent starting material for the synthesis of naturally occurring compounds [71, 72]. The monoepoxide limonene oxide, for example accessible using methyltrioxorhenium (MTO) and H_2O_2 as the oxidant, represents a precursor for high molecular weight polycarbonate which can by produced by copolymerisation with CO_2 [73]. The monoepoxide/diepoxide ratio is controllable through the choice of solvent, temperature, and starting material concentrations. Using CH_2Cl_2 as the solvent, limonene can be converted completely to the monoepoxides within 30 min at room temperature [18]. Treating limonene under Wacker conditions ($PdCl_2/CuCl_2/LiCl$), the allylic position becomes accessible for the introduction of an oxygen functionality (Fig. 6.5) [74]. The main product of the Wacker oxidation of limonene is carvenyl acetate, which is formed in 87% in the presence of HOAc and O_2 (1 bar) at 80 °C after 3 h.

Using MTO (methyltrioxo rhenium, CH_3ReO_3), also bicyclic monoterpenes such as α-pinene, β-pinene, camphene, and carene can be oxidised. α-Pinene can be found in concentrations up to 80% in pine oil and is a precursor for several compounds (Fig. 6.6). The epoxide of α-pinene represents the starting material for the synthesis of campholenic aldehyde [75]. Verbenols, which are used as ingredients in plant protection products and the odour verbenone, are also accessible from α-pinene. Oxidation of α-pinene using 0.13 mol% of the complex [Co(4-methylpyridin)$_2$Br$_2$], and O_2 lead to 76% of verbenone within 7 days [76].

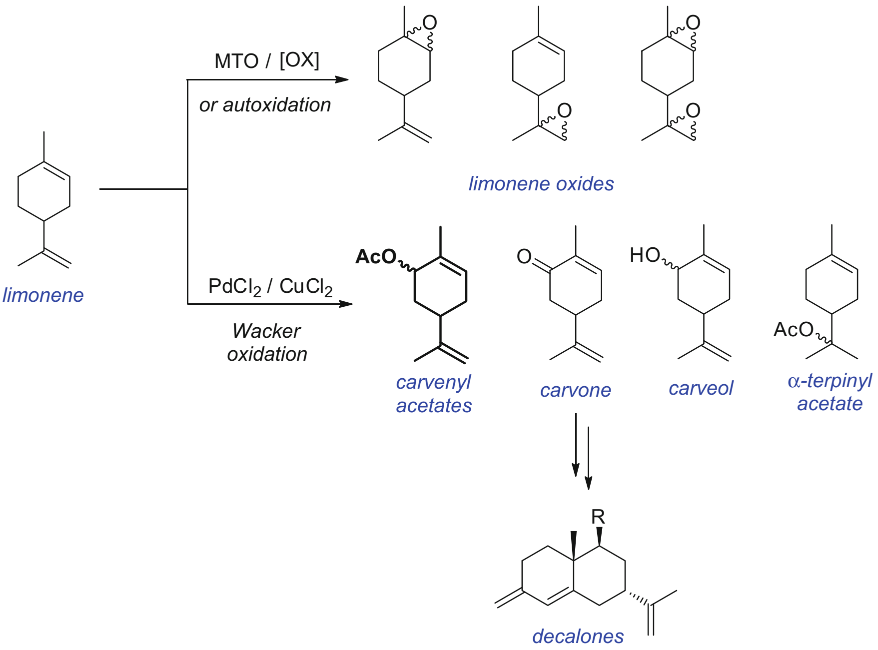

Fig. 6.5 Oxidative modification of limonene

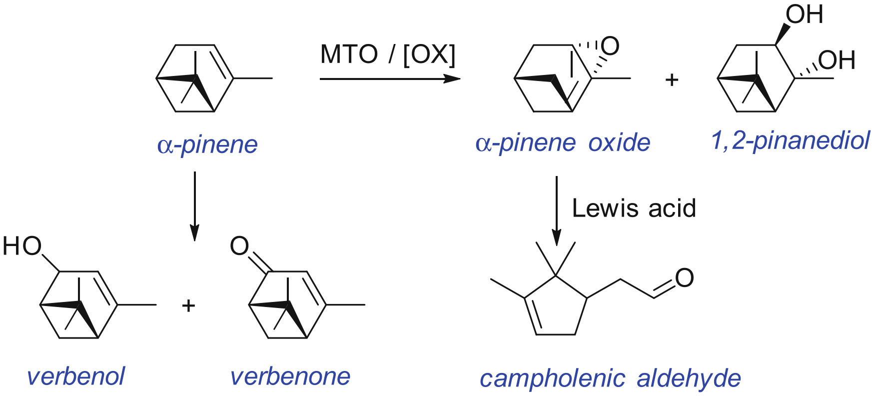

Fig. 6.6 Oxidative modification of α-pinene [77]

Oxidation protocols can further be applied on terpene alcohols, which are exemplarily mentioned with geraniol, one of the most important monoterpene alcohols together with linalool and present in many essential oils. The following example (Fig. 6.7) demonstrates the selective radical oxidation of geraniol using 5 mol% TEMPO (2,2,6,6-Tetramethyl-piperidin-1-oxyl) and 0.5 mol% Cu in the presence of O_2 [78]. The odour geranial is mostly applied in the cosmetic industry.

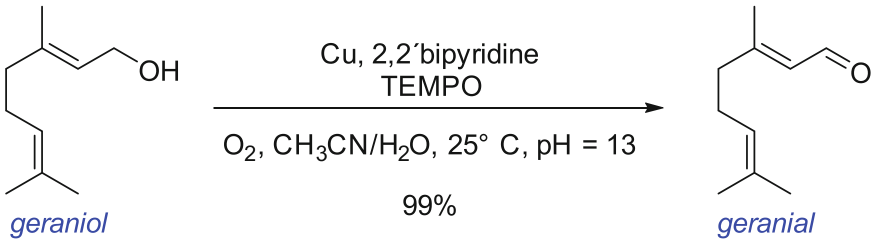

Fig. 6.7 Environmentally friendly synthesis of the odour geranial

6.4 Lignin and Phenylpropanoids

Lignin represents one of the few abundant renewables with an aromatic scaffold of phenylpropane units. For the valorisation of these highly cross-linked natural polymers, investigation of its molecular structure is necessary, which is often an analytical challenge. Lignin sources are heterogeneous by nature, and therefore, the obtained monomers also differ depending on the pretreatment. The complexity of this amorphous macromolecule stimulates the development of robust and versatile degradation/functionalisation methods, for example selective oxidations [79, 80].

Several catalytic methods applied so far to oxidise the renewable source of aromatic compounds. Inorganic catalysts, such as methyltrioxo rhenium (MTO), salen complexes (e.g. Cobalt-Schiff base complexes), vanadium complexes, or polyoxometalates (POMs) (polyoxometallates) achieve an efficient degradation of lignin and lignin model compounds. In relation to other catalysts, MTO represents a quite simple structure that activates molecular oxygen or hydrogen peroxide, whereas with the latter one, also challenging substrates such as activated phenols can be oxidatively upgraded [58, 59]. The excellent reactivity involves overoxidation leading to an increase in functionalisation of the material which might be a useful side effect. An advantage of the salen complex method is its compatibility with aqueous reaction media [81]. Cobalt-Schiff base complexes are able to reversibly react with O_2 [79]. Modifying the ligands, sterical demand allows to control the oxidation range of lignin. Metal-free organocatalytic systems (for example, TEMPO in combination with NaBr and NaClO), photocatalytic and electrocatalytic oxidations provide a useful alternative to conventional oxidation methods [82]. Biomimetic catalysts also offer appropriate reactivities, for example metal porphyrins [79]. They imitate enzymes (peroxide-dependant ligninase or laccase) which naturally occur in several white-rot fungi [83, 84].

One of the most established products out of an oxidative degradation of lignin is vanillin (4-hydroxy-3-methoxybenzaldehyde), a key intermediate for the synthesis of bio-based polymers. It is likewise used as a flavouring and fragrance ingredient in food and cosmetic industries [85]. Nowadays, 15% of the overall vanillin production originates from lignin [86]. It is treated with oxidants in an aqueous alkaline solution at pH under high temperatures and pressures. Possible products of this

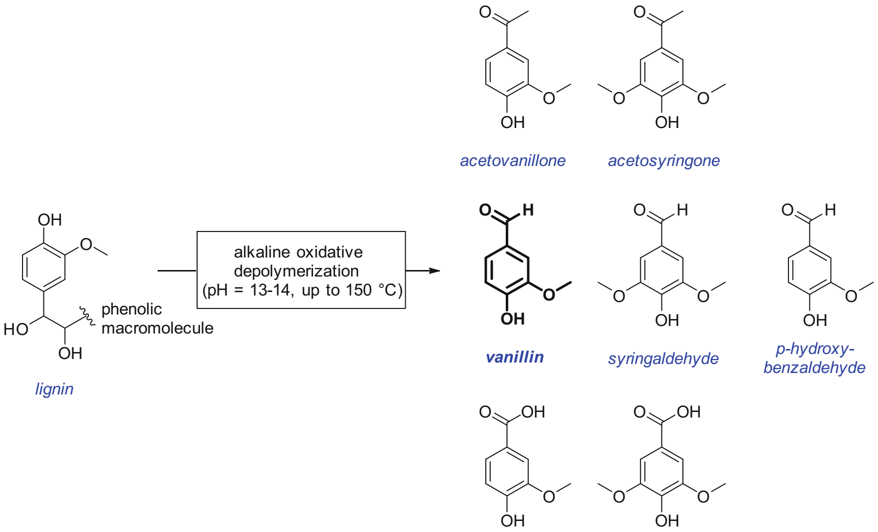

Fig. 6.8 Ketones, aldehydes, and carboxylic acids from lignin after alkaline oxidative treatment

depolymerisation are shown in Fig. 6.8. While developing a mechanism of the alkaline oxidation reaction starting from the lignin polymer is not a straightforward task [79], the oxidative C–C bond cleavage of the lignin model compound isoeugenol is well described. The isomerisation of the naturally occurring eugenol in the presence of KOH at 250 °C followed by oxidation with $KMnO_4/O_3$ has for a long time been the main industrial process for the production of vanillin, but got nowadays outperformed by the conventional vanillin production based on lignin [87, 88].

6.5 Conclusions

This chapter provides an overview of industrially relevant oxidation reaction of renewables which represents a powerful strategy for the incorporation of renewables into the chemical value chain and becoming an alternative for petrochemical-based processes. The target and research focus should be on fulfilling the restrictions of green chemistry which asks to perform oxidations in selective, non-toxic, and resource-efficient catalytic processes. Thus, present catalyst systems need to be optimised, particularly towards catalyst recycling as well as the usage of molecular oxygen to observe an overall low C:O ratio.

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Chapter 7
Tandem Reactions with Renewables

T. Seidensticker, K.A. Ostrowski and Andreas J. Vorholt

7.1 Introduction

Tandem catalytic reactions and related processes offer major benefits in comparison with the stepwise synthesis of intermediates and valuable chemicals. Hence, various investigations have been conducted during the last years aiming for the development of selective tandem catalytic systems in numerous chemical disciplines [1–8]. Generally, in tandem systems, two or more individual chemical transformations are merged together, which minimises on the one hand time and effort. On the other hand, also resources can effectively be preserved which is very attractive with respect to both economic and ecologic aspects. In particular on an industrial scale, this becomes increasingly important as sustainability is crucial for future chemical production processes.

Thus, the idea of tandem catalytic systems, i.e. two or more distinct chemical reactions taking place in a single vessel, not requiring work-up or purifications in between, fits the concept of “Green Chemistry”. These twelve principles primarily suggested by Anastas and Warner [9–11] encourage chemists for developing sustainable processes and thereby minimising waste and hazardous substances. The combination of at least four green chemistry principles is achieved by combining tandem catalytic systems with renewables. This is waste prevention by not isolating intermediates, using atom economic catalysis to ensure all used materials are incorporated into the final product and no stoichiometric reagents are applied, and the substrates used are from renewable resources. Hence, the incorporation of tandem catalysis into renewables offers one possibility for turning chemical production more sustainable in the future [12].

The general concept for combining two or more chemical transformations into one process has attracted the effort of many researchers. Nevertheless, it seems, as if no, or only little, consensus concerning an uniform and generally accepted taxonomy of such systems has gained acceptance [13–16]. This fact impedes the search for related literature, mainly because similar approaches are termed differently or

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different concepts are named the same. In some examples, in which the incorporation of tandem concepts was not the main target, designations are even completely omitted.

Nevertheless, several reviews appeared in this field with respect to the different catalysts applied, e.g. organocatalyst [17–19], transition metal [20–24], and enzymes [25, 26]. There are also different reviews present that focus on only one concept, and different classifications have been proposed, e.g. “multicatalysis” or “cooperative multicatalyst systems” [19, 27–29], “concurrent tandem catalysis” (also “domino catalysis”), and “sequential” or “consecutive” catalysis [1, 2, 30, 31].

In general, three main reactions patterns can be attributed to “tandem catalysis”. They all have three aspects in common, that is:

- Two or more individual chemical transformations take place.
- Each reaction contributes to the formation of the final product.
- No intermittent isolation or work-up procedures are required.

These three categories are [14] (Fig. 7.1) as follows:

- *orthogonal tandem*,
- *auto-tandem*,
- *assisted tandem*.

Their taxonomy as well as advantages and disadvantages have been introduced and thoroughly discussed by dos Santos and Fogg in their detailed review [14].

On the one hand, if two different catalysts operate side by side, each of them responsible for one specific transformation, an *orthogonal tandem* system is present. In the other scenario, i.e. *auto-tandem* catalysis, one catalytically active centre promotes two or more different reactions without the need for any intervention. In these two tandem catalytic set-ups, the substrates and reaction conditions for each reaction step are present from the outset and no alteration is of need. Opposed to these two examples, a tandem catalytic reaction is conceivable, in which the final

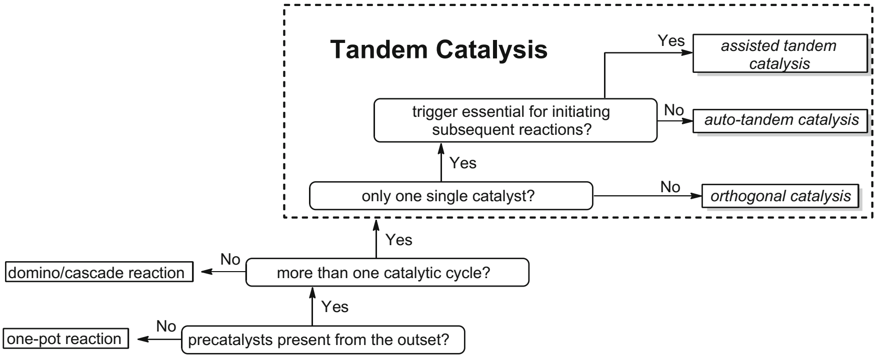


Fig. 7.1 Classification of tandem catalytic systems in the context of sequential transformations [14]

reactions steps of a catalytic sequence only occur, if the conditions are altered or a new substrate/reagent is added. This is called *assisted tandem* catalysis, and the catalyst may be changed in that way that it is no longer able to promote the previous reaction.

These three categories of tandem catalysis have to be interpreted in the general context of sequential elaborations of a substrate, in which several catalytic transformations are required. If the catalyst for each step is added after the previous reaction is completed, the sequence is called one-pot reaction. In a domino process, one catalyst promotes several (almost) identical transformations, i.e. only one general catalytic mechanism is present (e.g. oligomerisation of ethene).

In this chapter, the taxonomy as defined by Fogg and dos Santos will be used to evaluate the different concepts applied in the presented examples. Domino processes, as defined by Tietze et al. will not be discussed, as these usually need highly activated substrates [3, 13]. Hence, this concept rarely seems compatible for transforming renewable substrates. Nevertheless, it has to be mentioned that there are numerous beautiful examples following this remarkable concept, including several total syntheses and asymmetric reactions [5, 7, 8, 17, 18, 27, 32–34].

Regarding all of the aforementioned concepts of sequential catalysis, it has to be stated that the essential character of each approach is to minimise work-up and purification procedures and thereby representing an alternative to stepwise synthesis and its inherent disadvantages. In combination with renewables, these ideas of merging transformations with sequential catalysis in all of the presented variations contribute essentially to sustainability or “Green Chemistry”. Concerning this, the superiority of a sequence as a whole is way more significant than to distinguish between the different concepts of sequential tandem catalysis [35].

In this chapter, the focus is set on all those approaches for the transformation of renewables, in which the substrate undergoes sequential homogeneous catalytic transformation, without intermittent purification or work-up interventions. These reaction set-ups will be classified according to the taxonomy of Fogg and dos Santos as presented earlier. Additionally, the authors focused mainly on selective transformation in homogeneous transition metal catalysis and towards technical relevance [36, 37]. Thermal-, light-, or radical-induced transformations will not be discussed. When gathering publications fitting this scope, the authors worked out that renewables derived from oleo compounds [38], terpenes and phenylpropanoids, are most abundant in tandem catalysis. Selective transformation of carbohydrates and lignocellulose in tandem reactions has yet just started. Furthermore, four main reactions have been worked out, which represent the pillars of tandem catalysis with renewables. Therefore, this chapter is subdivided into four parts, one for each reaction:

- Metathesis
- Hydroformylation
- Defunctionalisation
- Isomerisation.

To the best of the authors' knowledge, most of the important ideas for the sequential homogeneous catalytic transformation of renewables were taken into account. Nevertheless, the inconsistent nomenclature and the variety of possible substrates referred to as renewables make the comprehensive overview very challenging. Hence, the following chapter is inherently a subjective overview on the focused topic.

7.2 Tandem Reactions with Metathesis

The metathesis reaction varies the substituents of double bonds which are available for further modifications and functionalisations in possible tandem reaction sequences. Successful tandem protocols were achieved by an assisted tandem catalysis synthesising saturated bifunctional molecules from fatty esters. The key in this tandem catalysis is the application of ruthenium as catalyst being active in metathesis and hydrogenation reactions. The hydrogenation step subsequent to metathesis is induced by pressurising the reaction mixture with hydrogen. The residue ruthenium catalyst is active for the hydrogenation step but inactive for further metathesis reactions. Therefore, it is a big challenge to develop more stable catalysts, which catalyse both reaction steps without degeneration. An example of the cross-metathesis of terminal olefins is given in Fig. 7.2, which has the advantage of shifting the equilibrium to the right side by setting ethene free. The saturated compound is obtained by applying hydrogen pressure.

7.2.1 Cross-Metathesis

Bruneau and Dixneuf [39] showed different approaches yielding saturated C_{12}-amine-esters by cross-metathesis and subsequent hydrogenation of the double bond and the nitrile moiety (Fig. 7.3). In 2009, they explored the cross-metathesis of 10–undecyl methyl ester with acrylonitrile and a consecutive hydrogenation of the newly formed double bond of their cross-metathesis product (approach I) [40]. The highest activity in metathesis was achieved with the ruthenium catalyst "Grubbs-Hoveyda II". The linear, saturated amine compound is yielded by pressurising with hydrogen to induce the hydrogenation of the double bond and the nitrile group in the cross-metathesis product. Both reaction steps (metathesis and hydrogenation) of the

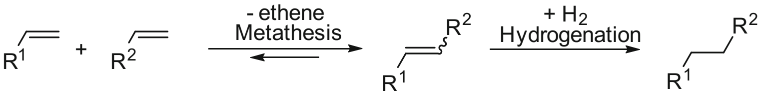


Fig. 7.2 General metathesis/hydrogenation of terminal olefins releasing ethene

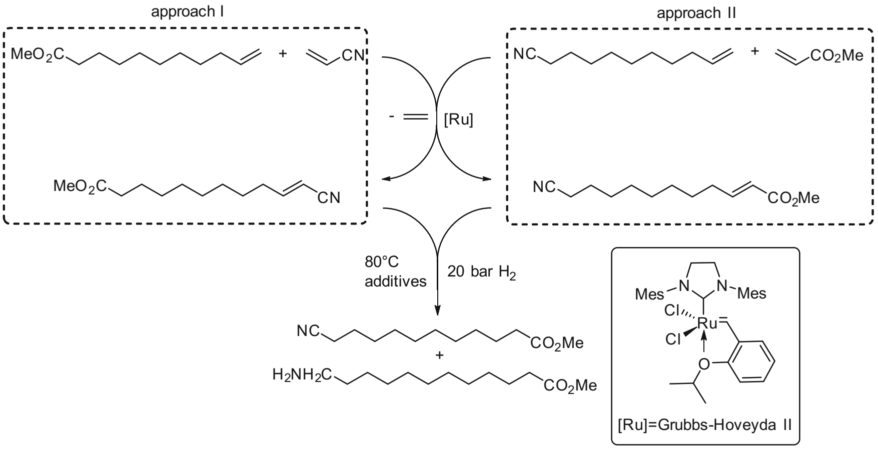


Fig. 7.3 Two approaches to saturated C_{12}-amine-esters by tandem catalysis with different substrates

tandem reaction were investigated autonomously from each other. A slow addition of the metathesis catalyst to the reaction solution favours the conversion of acrylonitrile with a TON of up to 1960. This TON is limited due to the deactivation of the catalyst in the presence of acrylonitrile [41]. Nitrile groups and double bonds are hydrogenated afterwards with the same catalyst and with other ruthenium–benzylidenes/ruthenium–indenylidenes catalysts obtaining up to 99% yield [42]. The so-synthesised linear bifunctional molecule carries an ester moiety as well as a primary amine which are used, e.g. in polyamides.

A further approach was made to yield these C_{12}–amine-esters by employing 10–undecene nitrile and methyl acrylate (approach II). Deactivation of the metathesis catalyst with 10–undecene nitrile is slower than with acrylonitrile; therefore, higher TONs of up to 17.200 were achieved using a continuous injection of the catalyst [43]. The metathesis step is completed after 1 h, and the hydrogenation of the nitrile moieties and the double bond was started in the presence of hydrogen pressure. The addition of ^{t}BuOK enhances the hydrogenation activity with a yield of up to 97% for the saturated amine product.

Dixneuf applied 2009 further ω-functionalised olefins for the synthesis of bifunctional molecules suiting well in polymer applications [44]. Undecylenic aldehyde was employed as a renewable to yield C_{20} unsaturated α,ω-dialdehydes in a self-metathesis reaction or, if acrolein is applied, C_{11} unsaturated α,ω-dialdehydes were gained in a cross-metathesis reaction catalysed by Grubbs-Hoveyda II (Fig. 7.4). The cross-metathesis of acrolein and undecylenic aldehyde shows high yields up to 78% after 18 h.

Hydrogenation converts these unsaturated dialdehydes into the saturated diols catalysed by the same catalyst. The hydrogenation of the double bonds and the

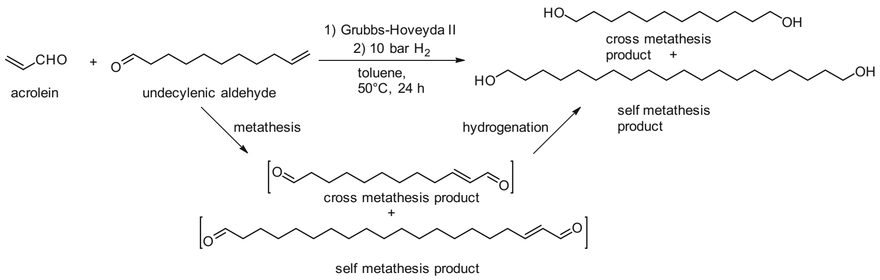


Fig. 7.4 Acrolein in a metathesis/hydrogenation tandem catalysis

reduction in the aldehydes were initiated by addition of hydrogen gas. Similar yields up to 72% were isolated for both diols.

7.2.2 *Intramolecular Ring-Closing Metathesis*

This elucidated assisted tandem reaction of metathesis and hydrogenation is transferable to more specific and functionalised fatty acids. Fischmeister and Bruneau investigated the intramolecular ring-closing metathesis of different compounds derived from methyl ricinoleate [45]. They synthesised various allylic ether compounds and an acrylic ester using these as starting material in tandem catalysis. Two examples are shown in Fig. 7.5. The intramolecular ring-closing metathesis using Grubbs-Hoveyada II and a consecutive hydrogenation give excellent yields of up to 92% for the saturated ether product. This two-stage tandem reaction opens the access to valuable tetrahydropyrans, saturated esters, and diesters. The transferation to the acrylic ester derivative of methyl ricinoleate yields a lactone which is valuable, e.g. as monomer. In summary, important classes of pyrans and bifunctional molecules are accessible by this tandem catalysis. The complex synthesis of the starting material, which is not atom efficient in case of acrylic esters (HCl as by-product), is a serious drawback.

7.3 Tandem Reactions with Hydroformylations

The hydroformylation furnishes in general aldehydes from olefins. Therefore, a hydroformylation of renewables, e.g. fatty acids and terpenes, gives bifunctional molecules with ester and aldehyde moieties (see Chap. 3). These aldehydes represent reactive intermediates allowing further modifications. Hydroformylation can be an essential key step in tandem processes of renewables, mostly unsaturated fatty acids and terpenes, yielding valuable products [21].

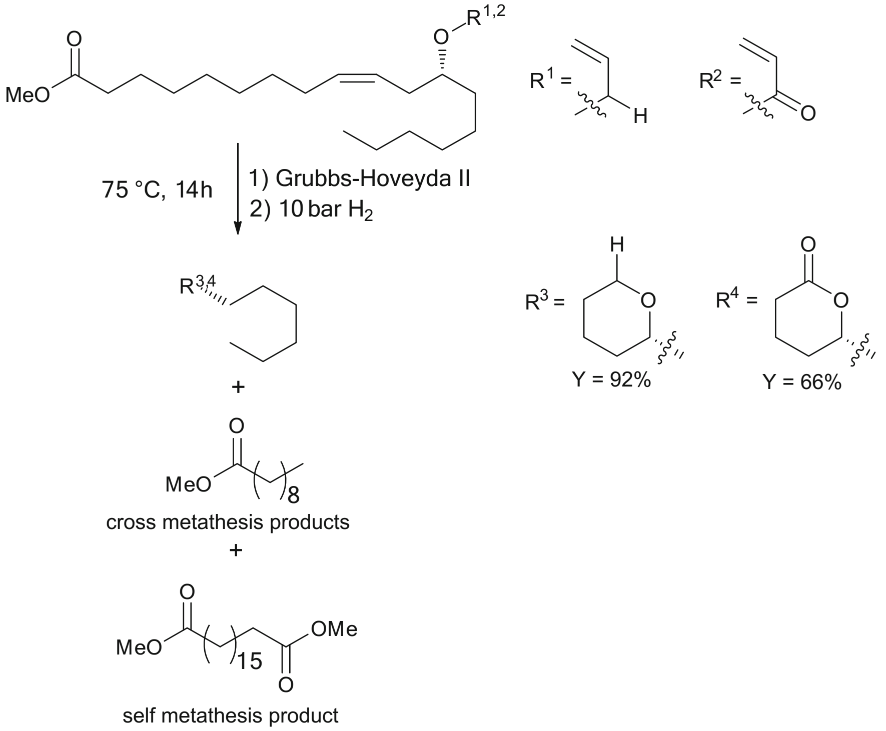


Fig. 7.5 Intramolecular ring-closing metathesis and hydrogenation in an assisted tandem catalysis

7.3.1 Hydroformylation/Hydrogenation

Hydrogenation of aldehydes produced by hydroformylation to the corresponding alcohols is one of the most important consecutive reactions for hydroformylation [46]. In early times of hydroformylation investigations, it was often an unintended reaction. In contrast to the assisted metathesis/hydrogenation tandem catalysis, the hydroformylation/hydrogenation is an auto-tandem catalysis. Therefore, the applied catalyst does not require further modifications being active in both catalyses.

Frankel et al. applied a broad range of fatty acids in hydroformylation reactions. It is temperature-dependent, in which the end-products are obtained, yielding aldehydes at low temperatures and alcohols at high temperatures. Starting from methyl linoleate, they yielded selectively 87% of the branched alcohol in 4 h using $CO_2(CO)_8$ as a precursor (Fig. 7.6) under high temperatures (175–190 °C) [47]. The transition metal complex catalyses two different reactions (hydroformylation and aldehyde reduction) at a time generating saturated branched alcohol esters in auto-tandem catalysis. These products possess an alcohol moiety and an ester moiety, which are interesting for branched polyester applications. Applying methyl oleate and the same precursor with a phosphorus ligand at higher syngas pressure,

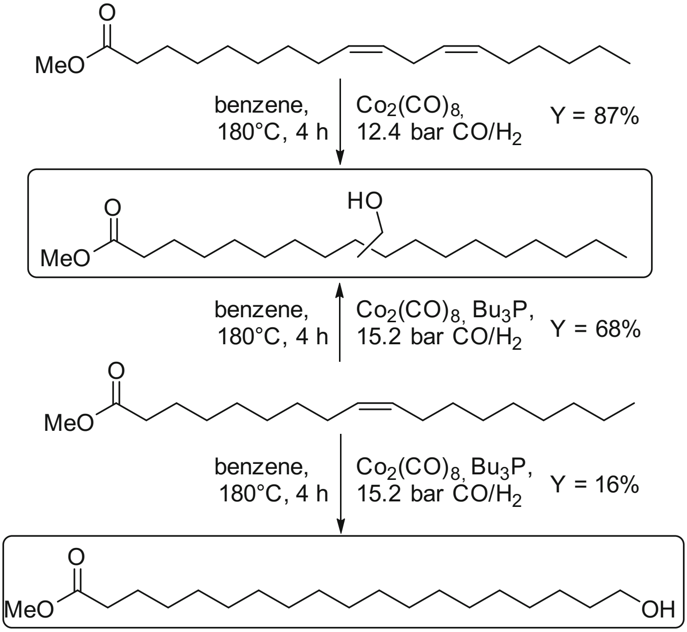


Fig. 7.6 Methyl linoleate and methyl oleate in tandem catalysis yielding alcohols

up to 16% linear besides 68% branched alcohols could be observed. This slightly different tandem catalysis yields a linear alcohol due to an isomerisation of the double bond to the terminal position, where it is hydroformylated and subsequently hydrogenated to the corresponding alcohol within three reactions.

This tandem catalytic protocol catalysing the hydroformylation and hydrogenation can be transferred to other renewables, e.g. terpenes. Clement and Orchin applied different terpenes, such as limonene, myrcene, β-pinene, and β-terpinene, yielding saturated alcohols after hydroformylation and hydrogenation in tandem catalysis. As seen before, $CO_2(CO)_8$ was used as catalyst at high temperatures of 150 °C. These alcohol products can be applied, e.g. as fragrances due to their structural similarity with other fragrances [48].

7.3.2 Hydroformylation and C–O Bond Formation

7.3.2.1 Intermolecular Hydroformylation/Acetalisation

The deliberate choice of solvents and catalysts in hydroformylation can result in a consecutive acetalisation of the formed aldehyde. These acetals are used, for example, as a protected form of aldehydes in organic synthesis or they find applications as solvents and additives in fuels. A simple and common way of

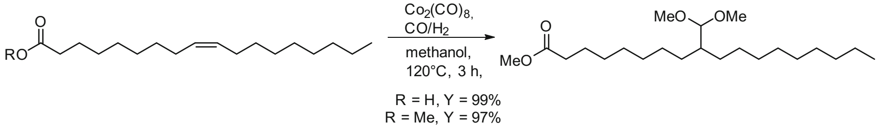


Fig. 7.7 Hydroformylation of oleic acid with subsequent acetalisation in a tandem catalysis

producing those acetals is carrying out a hydroformylation in alcohols or triethyl orthoformate as solvent serving as an alkoxy source for the acetalisation in a tandem catalysis.

The application of oleic acid or methyl oleate in methanol in the presence of a cobalt catalyst was presented by Frankel and it leads to very high yields of 99% distillable product in 3 h. Simultaneously, an esterification of the carboxylic acid with methanol takes place yielding the same methyl ester product independently of the choice of the substrate (Fig. 7.7). These products potentially serve as polyvinyl chloride plasticisers [49].

In ethanol, Gusevskaya observed selectivities up to 90% of diethyl acetals for various terpenes (α-terpinene, γ-terpinene, terpinolene, limonene) [50]. The subsequent acetalisation of the hydroformylation product is promoted by phosphite ligands [51]. Corresponding acetals have already been reported as side products with β−terpinene and limonene by Clement and Orchin [48]. Additionally, 3-carene, 2-carene, β-pinene, and α-pinene were converted into ethanol as well yielding up to 76% acetals with a very good selectivity of 82%. It was shown that the ligand $P(O\text{-}o\text{-}^t\text{BuPh})_3$ increases the acetalisation activity and accelerating the hydroformylation [52]. These acetals have potential as fragrances.

Kalck et al. converted *iso*-limonene and β-pinene into the corresponding ethyl acetals in triethyl orthoformate as solvent with good yields of up to 76% (Fig. 7.8) [53].

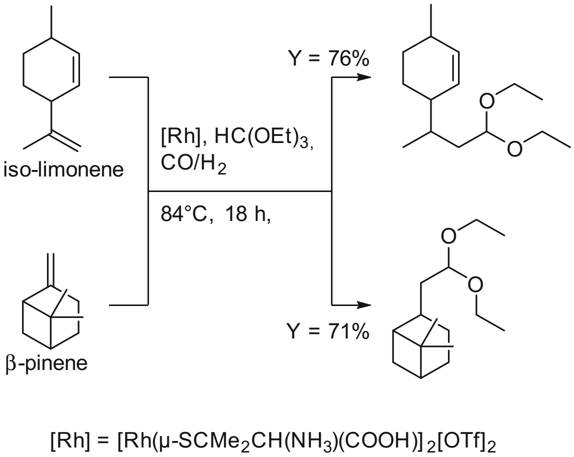


Fig. 7.8 Applying *iso*-limonene and β-pinene in hydroformylation/acetalisation

A ruthenium-based catalytic system for the formation of acetals under hydroformylation conditions with glycerol as renewable feedstock has been presented by Norinder et al. [54]. In the reaction of 1-octene, acetic acid as promotor and in ionic liquids, the desired five- and six-ring acetals have been formed in up to 95% yield after 20 h at 140 °C.

7.3.2.2 Intramolecular Hydroformylation/Lactolisation

Another way for a C–O linkage is an intramolecular lactolisation. Herein, aldehyde moieties, as the result from hydroformylation of olefins, and an alcohol moiety already present in the starting material undergo an lactolisation. Subsequently, this cyclic hemiacetal is converted into an unsaturated heterocycle by elimination of water. Mostly, the lactolisation and condensation steps are not catalysed by the applied metal complex displaying a tandem reaction opposed to tandem catalysis.

The group of Eilbracht explored two ways for the production of the cyclic vinyl ether displayed in Fig. 7.9. Starting with the hydroformylation of the terpene isopulegol, a lactolisation occurs afterwards as already observed in the investigations of Kalck [55] et al. and Chalk [56]. Elimination of water leads to the cyclic vinyl ether with a moderate yield of 59% after these three steps in one tandem reaction. If applying geraniolene (non-terpene), the same product was yielded in tandem catalysis within five reaction steps (first hydroformylation of the terminal double bond to the linear aldehyde, intramolecular cyclisation, second hydroformylation of the remaining double bond, lactolisation, and condensation of water) [57]. Kalck could yield the intermediate lactol from isopulegol with good yields of 79% without eliminating water [55]. Hence, the elimination of water can be controlled depending on the chosen reaction conditions, low syngas pressure at 78 °C and $[Rh(\mu\text{–}S^tBu)(CO)(P(OPh)_3)]_2$ as precursor favours the lactol over the corresponding dehydrated cyclic vinyl ether product which is formed to 5%.

Linalool was applied by Chalk in a comparable tandem reaction yielding the lactol presented in (Fig. 7.10). A very good yield of 87% and an excellent selectivity of 96% were achieved in the two-step tandem reaction. In this case, the

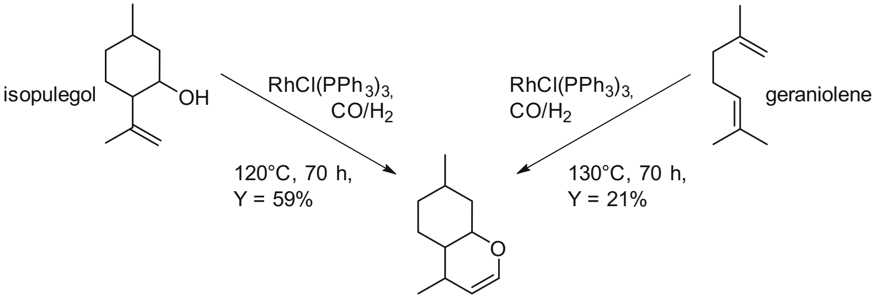


Fig. 7.9 Tandem catalytic approaches from isopulegol and geraniolene to a cyclic vinyl ether product

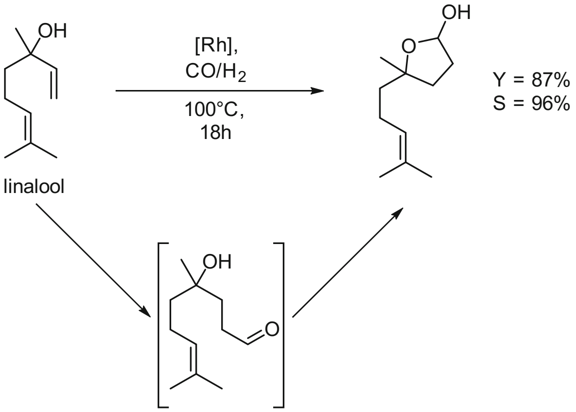


Fig. 7.10 Hydroformylation/lactolisation of linalool

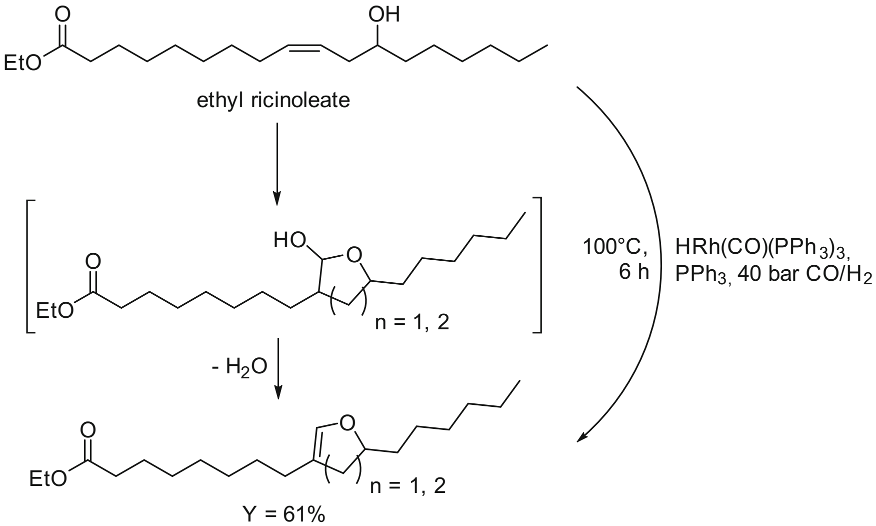


Fig. 7.11 Furanisation/pyranisation of ethyl ricinolate in a tandem reaction under hydroformylation conditions

corresponding dihydrofuran, which possibly formed due to an elimination of water, was not observed [56].

Furlan Mendes et al. explored the hydroformylation of castor oil and ethyl ricinoleate. They obtained cyclic products such as furan- and pyran derivates by hydroformylation, lactolisation, and condensation with yields for cyclic ethers of up to 61% for ethyl ricinolate and 74% for castor oil as the starting material, respectively (Fig. 7.11) [58]. It was proven that no metal catalyst is needed for the second step of the tandem reaction (furanisation/pyranisation step).

7.3.3 Hydroformylation and C–C Bond Formation

7.3.3.1 Hydroformylation/Cyclisation

The carbonyl function formed by the hydroformylation of olefins is electrophilic, wherefore a rearrangement can lead to intramolecular cyclisation reactions, as already seen before for the lactol formation.

Gusevskaya et al. developed a pathway for the conversion of limonene into its secondary alcohol in a tandem system consisting of hydroformylation and a C–C-bond forming cyclisation as shown in Fig. 7.12. The product and its derivatives can be used as fragrances. The authors applied a bimetallic catalyst system with rarely used hydroformylation catalyst metals consisting of $PtCl_2$(DPPB) (DPPB = 1,4–bis(diphenylphosphino)butane) and $SnCl_2$. This rearrangement is promoted by the acidic nature of the catalyst system. After a quite long reaction time of 50 h, they yielded 80% of the desired product [59]. After closer investigations by the same group, they carried out the same reaction with a rhodium catalyst system and used pyridinium *p*–toluenesulfonate (PPTS) as co-catalyst for the cyclisation [60]. Besides higher yield of up to 96%, they achieved a stereoselectivity of product **a** with 3.6:1 in only 8 h.

7.3.3.2 Hydroformylation/Alkylation

The combination of a transition metal and an organocatalyst in tandem sequence with renewables was presented by Behr and Christmann [61]. They applied a known rhodium catalyst system for the hydroformylation and used the chiral

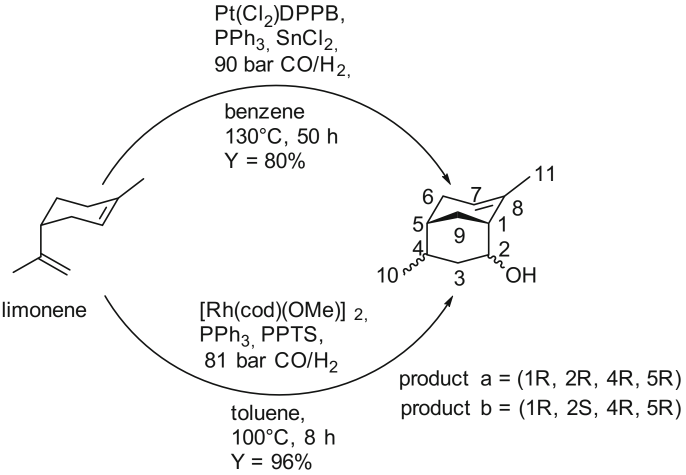


Fig. 7.12 Different approaches from limonene to a fragrance with high stereoselectivity

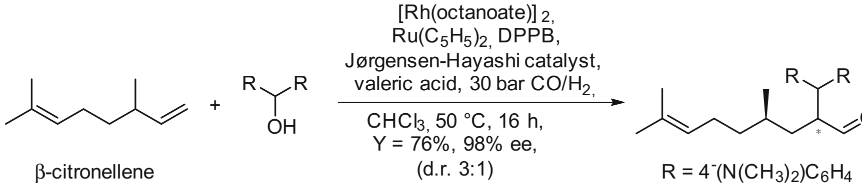


Fig. 7.13 Highly enantioselective tandem hydroformylation/alkylation of *β*-citronellene

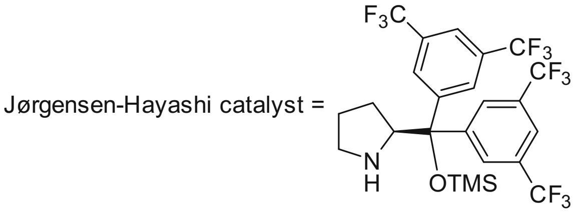


Fig. 7.14 Jørgensen–Hayashi catalyst for organocatalysis

Jørgensen-Hayashi organocatalyst (Fig. 7.14) for the asymmetric organocatalysed α-alkylation of the intermediate aldehyde. This orthogonal tandem catalysis leads from the monoterpene *β*-citronellene to the alkylated product with an excellent enantiomeric excess (ee) of 98%, a diastereomeric ratio (d.r.) of 3:1 and a good yield of 76% (Fig. 7.13). This developed asymmetric tandem catalytic system operates under quite harsh conditions for the organocatalyst, wherein higher temperature (up to 100 °C) and different substrates were applied.

7.3.3.3 Hydroformylation/Aldol Condensation

The tandem catalysis of hydroformylation and aldol condensation describes a possible way converting olefins into α,β-unsaturated aldehydes, which constitute an important class of fine chemicals. Beller and co-workers applied a broad range of olefins with citronellene as a renewable among them (Fig. 7.15) [62]. They used an orthogonal catalyst system consisting of the metal part: $Rh(CO)_2(acac)$ with NAPHOS (=2,2′ bis((diphenyphosphino)methyl)-1,1′-binaphthyl)) for the hydroformylation of citronellene, and the organocatalytic part: pyrrolidine with benzoic

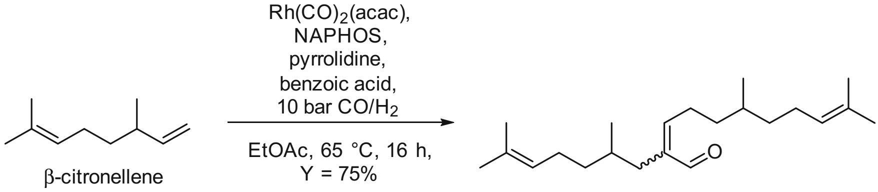


Fig. 7.15 Gaining α,β-unsaturated aldehydes in the tandem hydroformylation/aldol condensation

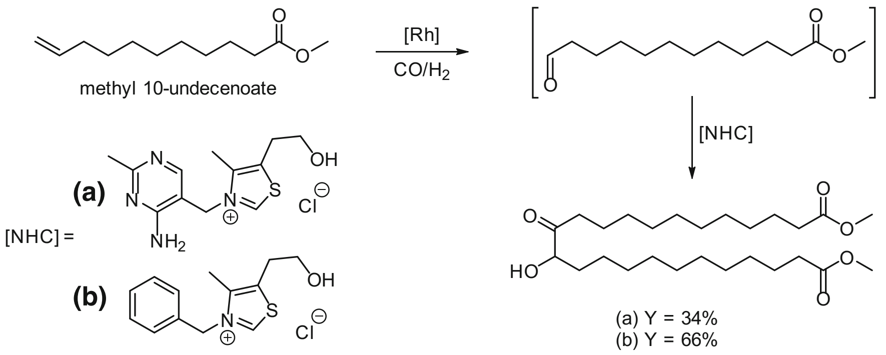


Fig. 7.16 Hydroformylation/acyloin reaction tandem catalysis with methyl 10-undeceonate for diester synthesis; **a** [Rh] = [Rh(acac)$(CO)_2$]/Biphephos, NHC = Vitamin B_1/Et_3N; **b** [Rh] = [Rh (acac)$(CO)_2$]/NiXantphos, NHC = more stable thiamine derivative

acid for the homo-aldol condensation. This organocatalytic system has already been developed and successfully applied in the homo-aldol condensation of aliphatic aldehydes before by Ishikawa and Saito [63]. The presence of an acid catalyses the formation of more reactive enamines leading to higher reactivity and yields ($Y = 75\%$).

7.3.3.4 Hydroformylation/Acyloin reaction

Selectively coupling two aldehydes produced in situ by hydroformylation via an acyloin reaction gives access to linear dimeric products. This orthogonal tandem catalytic system has been initially developed by Vorholt et al. [64] and consists of a Rh-catalyst for hydroformylation and an NHC organocatalyst for acyloin reaction. The latter forms an α-hydroxy ketone from two aldehydes via Umpolung. The developed tandem catalytic system has been successfully applied to the renewable methyl 10-undecenoate to produce linear α,ω-diester (Fig. 7.16).

Under the initially developed conditions, the diester was yielded with 34% but with improved reaction conditions under application of a different ligand and NHC precursor in NMP instead of DMF and 90 °C instead of 60 °C, the yield drastically increased to satisfying 66% [65].

7.3.3.5 Hydroformylation/Arylation

Almeida et al. [66] published the first rhodium-catalysed arylation with aromatic boronic acids of aldehydes formed by hydroformylation in assisted tandem catalysis. In the first step, they applied β-pinene in a hydroformylation with [Rh(acac)$(CO)_2$] and triphenylphosphine as ligand. In the second step, the substrate phenyl boronic acid ($PhB(OH)_2$) was added to induce the rhodium catalysed arylation step

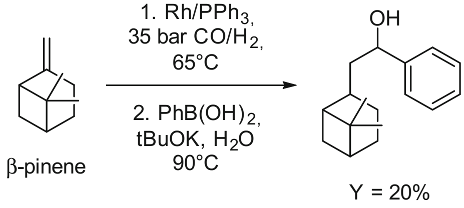


Fig. 7.17 *β*-pinene in a hydroformylation/arylation tandem system

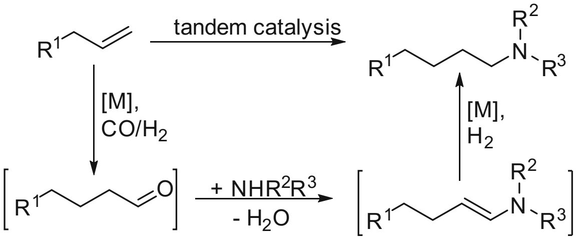


Fig. 7.18 Reaction pathway of the hydroaminomethylation with a secondary amine

at higher temperature. They yielded 20% product with an excellent chemoselectivity of 99% and high regioselectivity of 78% (Fig. 7.17). This tandem catalysis shows a simple way of producing secondary alcohols.

7.3.4 Hydroaminomethylation for C–N Bond Formation

The hydroaminomethylation (HAM) describes a three-step reaction sequence, wherein an alkene is hydroformylated to an aldehyde, followed by a condensation of an amine and a subsequent hydrogenation of the resulting enamine/imine forming an amine (Fig. 7.18). The first and the last reaction step are catalysed by the same catalyst complex displaying an auto-tandem catalysis. In general, aliphatic amines are important intermediates for industrial applications and are produced on large scales. The hydroaminomethylation as an atom economic tandem process forming amines from olefins is very attractive being superior to already established pathways with individual reaction steps.

Different primary and secondary amines have been applied in the hydroaminomethylation of fatty compounds which will be presented in the following. Behr et al. investigated the application of different amines in the HAM of ethyl oleate. Excellent results of 99% yield were obtained with morpholine for the tertiary amine [67] (Fig. 7.19). Amino acids are another class of interesting amines for the application in hydroaminomethylation reactions, which themselves can be attributed as renewable resources [68–70]. Therefore, interesting products were yielded with the amino acid derivative aspartic acid ethyl ester. About 68% triester product was generated being a potential crosslinker in polymers or an interesting precursor in the synthesis of surfactants. A high ratio of ethyl oleate to a primary

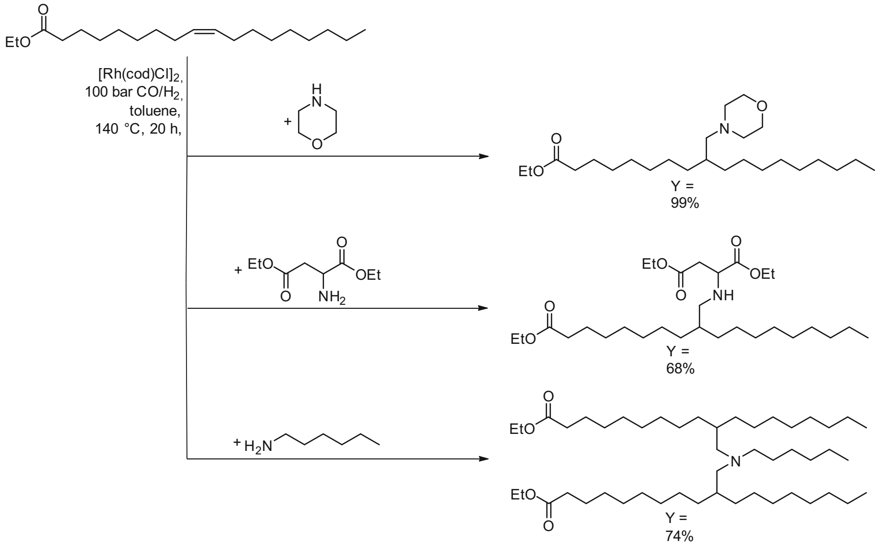


Fig. 7.19 Hydroaminomethylation of ethyl oleate with different amines

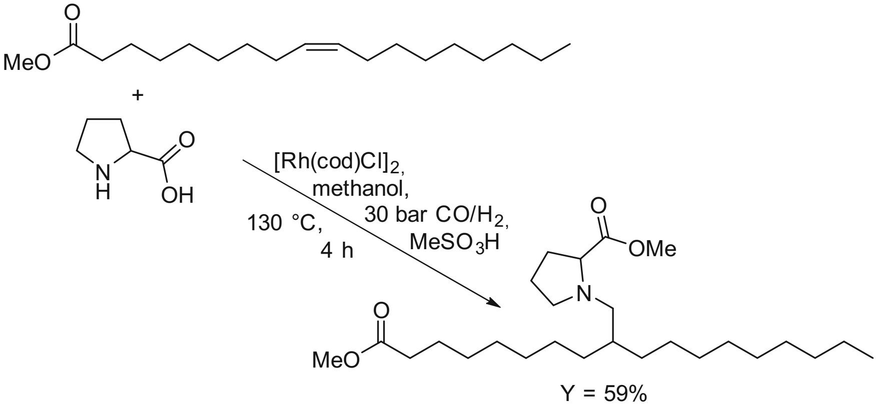


Fig. 7.20 Hydroaminomethylation of methyl oleate with proline

amine leads to a dihydroaminomethylation. Therefore, an excess of ethyl oleate in combination with the primary amine *n*-hexylamine yields a twofold condensation with the intermediate aldehydes. The corresponding dicarboxylic acid ester is synthesised in 74% yield. This branched structure with a diester functionality is attractive for polymeric synthesis or as precursors for cationic, anionic and amphoteric surfactants [67].

Another advantageous member of amino acids is proline, due to the secondary amino moiety. Vorholt et al. obtained a diester product from methyl oleate and

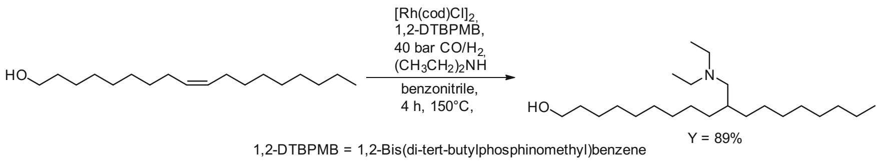


Fig. 7.21 Hydroaminomethylation of oleyl alcohol with diethylamine

proline with 59% yield in only 4 h (Fig. 7.20). In this tandem catalysis, the in situ esterification of the carboxylic group is an additional fourth reaction step, which occurs in one auto-tandem catalysis [71]. The used precious metal catalyst was successfully separated from the product and recycled in subsequent reactions by TMS technique (TMS = temperature-dependent multicomponent solvent). The latter describes a possible way for recycling applied catalysts. In TMS-systems, a single phase is formed at reaction temperature and a biphasic system is present at lower temperatures. Single-phase systems show no mass transport limitation and biphasic systems give the opportunity for a phase separation [72, 73].

Before, Eilbracht mentioned in a review article the possibility of the hydroaminomethylation of the amino acid derivative proline ethyl ester with 1-dodecene yielding 84% hydroaminomethylation product [21].

A further possible way to interesting surfactants via HAM with fatty compounds was shown by Vorholt et al. Oleyl alcohol and diethyl amine were applied yielding 89% product (Fig. 7.21). TMS techniques for recycling the transition metal precursor and the phosphorus ligand was also applied. The good surfactant properties of the product hinder a successful phase separation leading to an unsuccessful recycling of the catalyst [74].

Besides fatty compounds, terpenes were tested in detail. The conversion of limonene into different secondary and primary amines leads to valuable products which act as growth regulators for tobacco plants [75–77]. A representative molecule is the product displayed in Fig. 7.22 which was obtained in 93% yield by Eilbracht et al. from the HAM of limonene with morpholine [78].

The first ever reported example of hydroaminomethylation of oleo chemicals for the synthesis of potential polymer precursors for polycondensates was developed by Seidensticker et al. His initially developed protocol for the selective *bis*-hydroaminomethylation of linear aliphatic alkenes was successfully applied to the two renewables methyl 10-undecenoate for diester synthesis and 10-undecenol for diol synthesis, respectively [79]. Key to success is the implementation of the cyclic diamine piperazine, at which a twofold HAM of two independent olefins can occur and leads to a formal dimerisation (Fig. 7.23).

These compounds, the linear diester and the linear diol, have been proven recently to be convertible into a novel, piperazine-linked polyester with promising polymeric properties [80]. Additionally, in the rhodium-catalysed *bis*-HAM of the unsaturated ester, a selective crystallisation procedure of the product from the crude reaction mixture allowed for the recycling of the homogeneous catalyst.

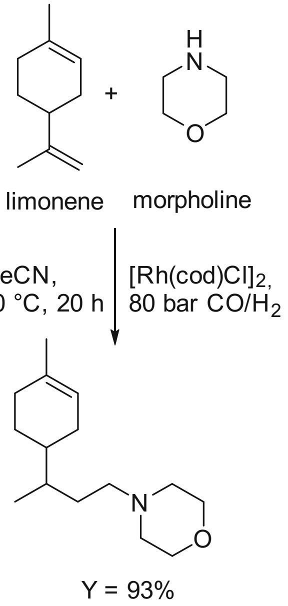


Fig. 7.22 Hydroaminomethylation of limonene with morpholine

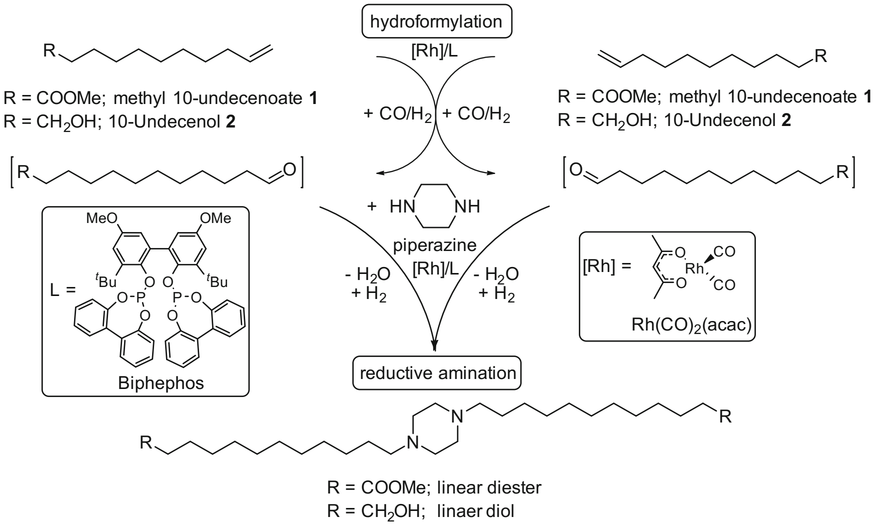


Fig. 7.23 *Bis*-Hydroaminomethylation of methyl 10-undecenoate and 10-undecenol with piperazine for the formation of a linear diester and a linear diol, respectively (Copyright Wiley-VCH Verlag GmbH & Co. KgaA. Reproduced with permission)

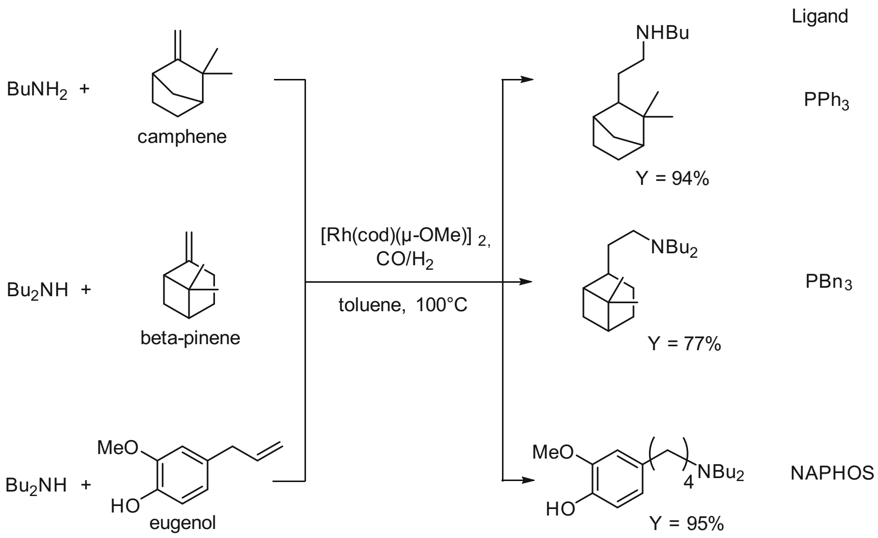


Fig. 7.24 Various terpenes and eugenol in hydroaminomethylation

Dos Santos et al.modified various terpenes and eugenol, a phenylpropanoid, via hydroaminomethylation (Fig. 7.24) [82, 83]. Excellent yields of 94% in a quiet long reaction time of 20 h with triphenylphosphine as cheap phosphorus ligand, from camphene with butylamine to the desired product were observed. A short reaction time of 4 h with PBn_3 as phosphorus ligand can be applied for yielding 77% for the product out of *β*-pinene with dibutylamine [82]. An excellent regioselectivity of up to >99 and 95% yield were obtained in 24 h for the linear product of eugenol using NAPHOS (=2,2′-bis((diphenyphosphino)methyl)-1,1′-binaphthyl) as bidentate phosphorus ligand and HOTf as acid [83].

Starting from the aldehyde or even from the alcohol, it is possible to yield saturated amines in one pot via different multiple tandem catalytic steps without hydroformylation. Bruneau et al. described a pathway from different saturated/unsaturated alcohols/aldehydes via reductive amination to the same saturated amines [84]. The conversion of different used terpenes (geraniol, nerol, citronellol, citronellal and citral) with *n*-butylamine lead in one pot to the same product within multihydrogen transfer processes catalysed by a ruthenium catalyst system. These different tandem catalyses consist of different catalytic steps (isomerisation, reduction, oxidation and hydrogenation) depending on the substrate, to afford a saturated aldehyde, which undergoes the reductive amination reaction (Fig. 7.25).

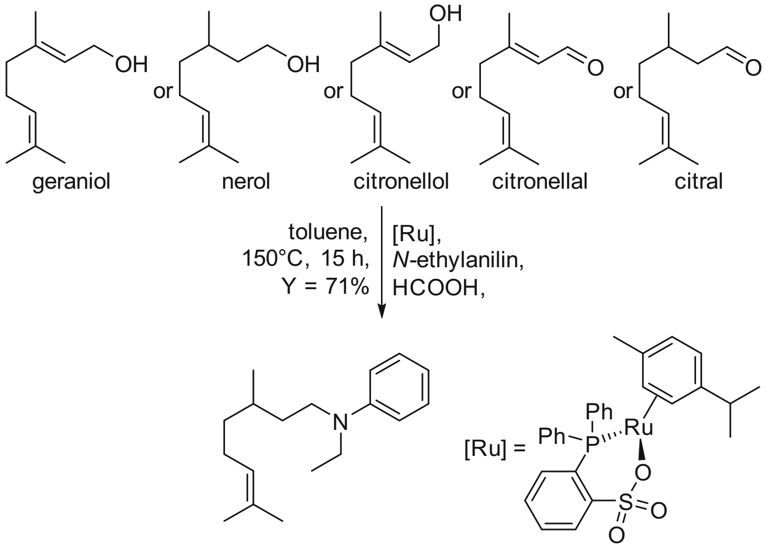


Fig. 7.25 Different starting molecules leading to the same compound by multiple tandem catalytic steps

7.3.5 *Alternative Syngas Resources for Hydroformylation*

The in situ generation of syngas followed by a hydroformylation still describes a rarely explored research field in chemistry. The substitution of carbon monoxide by the implementation of carbon dioxide addresses safety issues and turns the process more sustainable. Although carbon dioxide is not an agricultural product such as carbohydrates or fats and oils, it is often attributed as a renewable resource being present in our atmosphere [85–94]. Furthermore, a tremendous development of processes converting carbon dioxide to valuable chemicals and products can be observed due to the high impact on the greenhouse effect.

7.3.5.1 Reverse Water-Gas Shift Reaction (RWGS)

Carbon dioxide can be used as a substitute for carbon monoxide due to the equilibrium between the reverse water-gas shift reaction (RWGS) and the water-gas shift reaction (WGSR) as shown in Fig. 7.26. Either hydrogen from carbon monoxide and water or carbon monoxide from carbon dioxide and hydrogen can be generated for the in situ production of syngas in the laboratory.

Fig. 7.26 Equilibrium between RWGS and WGSR

$$CO_2 + H_2 \underset{\text{WGSR}}{\overset{\text{RWGS}}{\rightleftharpoons}} CO + H_2O$$

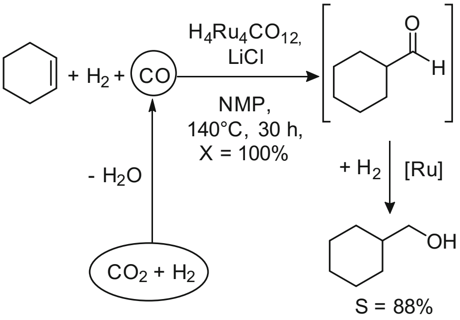


Fig. 7.27 Ruthenium-catalysed RWGS-reaction in tandem catalysis

Ruthenium carbonyl clusters were developed by Tominaga et al. catalysing the conversion of carbon dioxide into small molecules, e.g. methanol, methane and ethanol. These systems suffer from low selectivities, and the formation of these compounds seems to be more or less an instance of serendipity [95, 96]. These catalyses can in general be considered as tandem catalytic. Using Ru-complexes as catalysts, the selective hydrogenation of carbon dioxide to methanol has been improved [97]. The authors mentioned formic acid and its esters as intermediate products in this reaction, proving the presence of a tandem catalytic system. The combination of hydrogen and carbon dioxide has been shown to be a powerful tool for generating various different functional groups and molecules of value [98]. Tominaga et al. were the first who converted carbon dioxide to carbon monoxide in a RWGS for further reactions. They developed a subsequent hydroformylation of cyclohexene catalysed by a ruthenium species (Fig. 7.27). This represents an attractive alternative in comparison with the oxo-reaction (using CO/H_2) due to less toxicity of carbon dioxide compared to carbon monoxide [99].

The catalyst system based on the complex $H_4Ru_4CO_{12}$ is able to hydrogenate carbon dioxide and to catalyse the hydroformylation of alkenes to aldehydes (Fig. 7.27). The aldehyde is subsequently converted to the hydrogenated alcohol, because of the high hydrogenation activity of the catalyst system. Besides full conversion of cyclohexene, the overall selectivity of the alcohol product is 88% with only 2% of aldehyde left. The addition of LiCl almost completely suppresses the hydrogenation of the double bond in cyclohexene. Disadvantages are long reaction times of 30 h at high catalyst loadings. The same group investigated a recycling of the homogeneous catalyst by a biphasic solvent system consisting of ionic liquids (IL = [bmim]Cl) and toluene. The quantitative results are comparable (conversion of 1–hexene = 97% and selectivity for the alcohol = 87%), and a reuse of the catalyst phase is feasible [100].

Eilbracht et al. [101] investigated the RWGS reaction in the hydroaminomethylation (HAM) of olefins with secondary amines and aniline. They used carbon dioxide as a carbon monoxide source and optimised the reaction conditions for the four-step tandem catalytic system using cyclopentene and

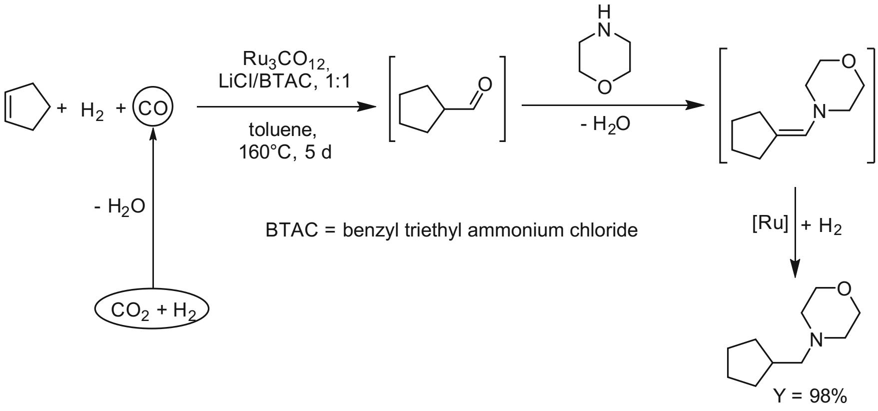


Fig. 7.28 Application of the RWGS in the hydroaminomethylation of cyclopentene with morpholine

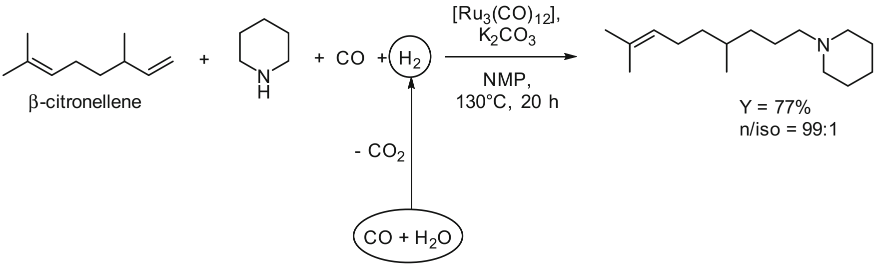


Fig. 7.29 Application of the WGSR in the ruthenium-catalysed hydroaminomethylation of *β*-citronellene

morpholine as a model system (Fig. 7.28). The authors yielded up to 98% HAM product for different alkenes after 5 d and employed LiCl/BTAC as "phase-transfer catalyst" to ensure sufficient solubility of LiCl.

Gülak et al. published a ruthenium-catalysed hydroaminomethylation of different functionalised olefins applying the WGSR, the opposite of the RWGS. Using carbon monoxide in water with base leads to the desired HAM products for different terminal olefins. A high yield of 77% and excellent regioselectivies for the linear amine were obtained by applying *β*-citronellene as a monoterpene. The remaining internal double bond remains intact, which is a result of the high chemoselectivity of this HAM for terminal double bonds (Fig. 7.29) [102].

7.3.5.2 Formic Acid Decomposition

The decomposition of formic acid (compare Sect. 2.2) produces thermally/catalytically carbon dioxide and hydrogen (Fig. 7.30). Applying formic

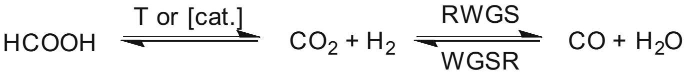


Fig. 7.30 Decomposition of formic acid leading to a RWGS

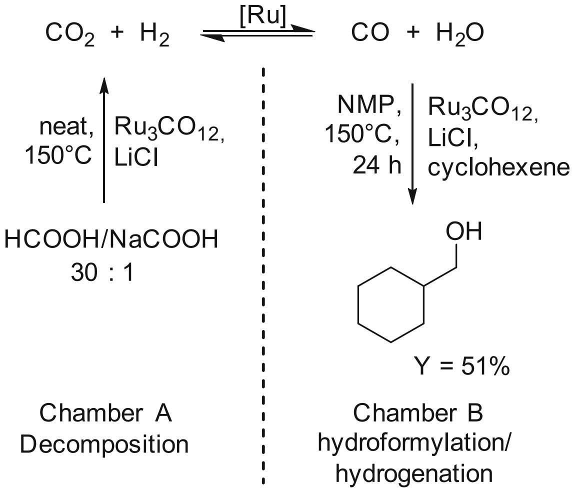


Fig. 7.31 Decomposition of formic acid and subsequent hydroformylation/hydrogenation in one tandem catalysis

acid as a CO_2 analogue addresses safety issues by not employing any gases simplifying the practical approach in the laboratory. This catalysed decomposition could be used as a tool applying formic acid for the hydroformylation of alkenes, again based on the concept of RWGS [103].

Porcheddu et al. reported a four-step tandem catalysis on carbon dioxide-based hydroformylation starting from formic acid as a source of CO_2 and H_2. The tandem catalysis consists of the decomposition of formic acid to CO_2 and H_2, a RWGS reaction to carbon monoxide, the hydroformylation with generated syngas to an aldehyde and the subsequent hydrogenation to an alcohol [104]. They realised this reaction sequence in a two-chamber reaction set-up, converting formic acid into the first chamber to yield up to 80 bar of hydrogen and carbon dioxide. This generated gas mixture was used in the second chamber to follow the aforementioned reaction sequence to yield 51% alcohol from cyclohexene (Fig. 7.31).

The application of ionic liquids resulted in high yields up to 86% for the desired alcohol, and they also showed the possible recycling of the Ru-catalyst system. In ionic liquids, they achieved a constant activity in five recycling steps for the decomposition reaction. They applied this reaction system successfully to linear, internal and aromatic alkenes.

7.3.5.3 Polyol Degradation

Another attempt to generate syngas is the total degradation of polypols, e.g. glycerol (Fig. 7.32). Due to the biodiesel production, there is an oversupply of glycerol being a co-product. Therefore, conversions of glycerol are very attractive.

Herein, a few approaches yielding syngas by reverse water-gas shift reaction (RWGS), by the decomposition of formic acid and by the degradation of polyols with a subsequent hydroformylation are presented.

Olsen and Madsen [105] developed a concept for the degradation of primary alcohols, which was used later on to fully degrade different polyols into syngas. Andersson et al. used this for the dehydrogenation/decarbonylation tandem reaction of polyol compounds such as *D*-mannitol, xylitol, *meso*-erythritol and glycerol [106]. They hydroformylated styrene with generated syngas derived from glycerol and other polyols in a two-chamber set-up. In the first chamber, glycerol is completely converted into carbon monoxide and hydrogen (=syngas) by an iridium catalyst. This stream of syngas was used in the second chamber for the rhodium-catalysed hydroformylation of styrene (Fig. 7.33). The degradation of polyols was conducted at high temperatures of 185–210 °C in high boiling solvents, such as mesitylene or diethylene glycol diethyl ether (DGDE) with a catalyst derived in situ from $[Ir(cod)Cl]_2$ and (*S*)-(−)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl ((*S*)–BINAP).

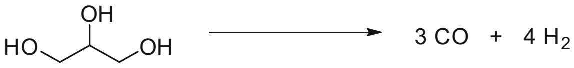


Fig. 7.32 Generating syngas from glycerol

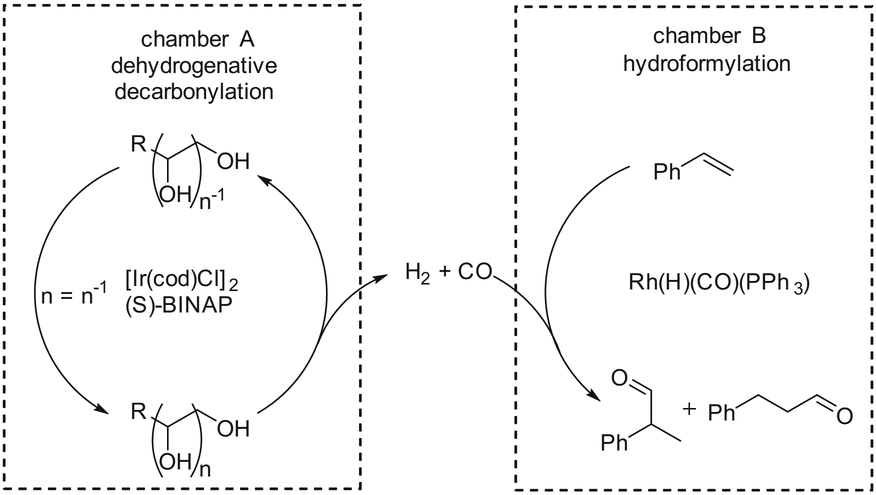


Fig. 7.33 Selective transfer of syngas from different polyols to styrene

7.4 Defunctionalisation—Overcoming Over-Functionalisation

Most processes in the organic chemical industry are based on simple unfunctionalised aliphatics and aromatics derived from fossil resources. Renewables in this case are generally “over functionalised”, as they incorporate inherently further functionalities. This usually hinders a one-to-one substitution of fossil resources in most applications and in already operating industrial processes. To address this and to turn renewables into more “suitable” compounds, efforts have been made to “defunctionalise” renewable resources.

7.4.1 Decarbonylative Dehydration

Linear aliphatic 1-alkenes are an important class of substrates for the production of plasticisers, lubricants, surfactants and as co-monomers for ethylene polymerisation. Often these are derived from oligomerisation of ethylene. A renewable access to ethylene, and hence to aliphatic 1-alkenes is, in principle, the dehydration of bio-sourced ethanol, but other renewable production routes to linear 1-alkenes are still highly desirable.

Fatty acids in this regard represent an important class of substrates for this purpose, as they possess in general highly linear alkyl chains. These are also inexpensive and readily derived from several natural sources. Additionally, 1-alkenes derived by decarbonylative dehydration (i.e. loss of one carbon atom) from renewable fatty acids are odd-numbered, since fatty acids typically contain an even number of carbon atoms. This special class of 1-alkenes is not accessible via oligomerisation of ethene and therefore highly valuable. Hence, several catalytic systems have been developed during the last decades for the production of linear 1-alkenes from fatty acids. The contributions are mainly based on the same catalytic cycle and have the loss of carbon monoxide and water in common. In the following, the development of decarbonylative dehydration of fatty acids as a tandem reaction is presented in historical order.

The first catalytic decarbonylative dehydrogenation of fatty acids has been reported by Foglia and Barr in 1976 using rhodium complexes as catalysts [107]. Stearic acid was almost completely converted into 1-heptadecene and its corresponding isomers (Fig. 7.34). The catalytic system consisted of Rh(III)Cl_3 at a

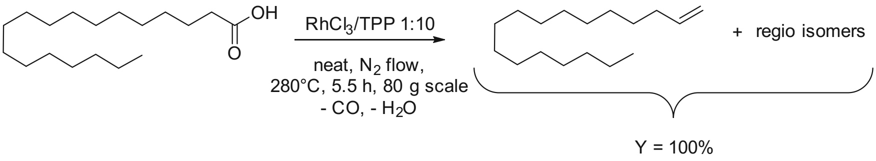


Fig. 7.34 Decarbonylative dehydration of stearic acid to heptadecenes

concentration of 1 mol% and triphenylphosphine as ligand in tenfold excess with respect to rhodium. No solvent was used at high temperatures of about 280 °C under a flow of nitrogen for effective removal of the gaseous reaction products.

Analysis of the gaseous reaction mixture showed the presence of carbon monoxide and water, proving the reaction is a decarbonylation–dehydration sequence rather than a decarboxylation process. Investigation of the reaction mechanism revealed that water is eliminated by the in situ formation of an anhydride, which oxidatively adds to the rhodium. Finally, carbon monoxide, the alkene and the corresponding acid are set free, and the active metal centre restarts the catalytic cycle.

The crucial role of anhydride formation as the preliminary step in the catalytic decarbonylative dehydration shows that two reactions operate side by side to furnish the desired 1-alkene. However, anhydride formation in this case is rather temperature-induced than a catalytic reaction. Hence, decarbonylative dehydration is rather a tandem reaction opposed to tandem catalysis.

Miller et al. built their investigations upon these findings and used anhydrides as promoters and improved the overall yield by directly distiling the α-olefin from the autoclave to avoid side reactions [108]. A palladium system consisting of [Pd $(TPP)_2Cl_2$] as precursor and additional TPP gave the best selectivities and TONs at a low concentration of only 0.01 mol%. Different saturated as well as unsaturated fatty acids, e.g. oleic acid, were converted into their corresponding 1-alkenes in very good yields with up to 97% without isomerisation. Either acetic or propionic anhydride in stoichiometric amounts were used to form in situ mixed anhydrides [109].

Later on, the protocol developed by Miller was used for the large-scale synthesis of 1-alkenes from various saturated as well as unsaturated fatty acids by Kraus et al. Applying the same reactions conditions but with linoleic acid as starting material, the authors were able to isolate the interesting triene 1,8,11-heptadecatriene in 69% yield [110].

To overcome the need for high reaction temperatures, Gooßen and co-workers developed a modified protocol for the decarbonylative dehydration [111]. Pivalic anhydride was used as promotor, with a catalyst system derived from $PdCl_2$ and DPEphos (=bis(2-diphenylphosphinophenyl)ether) in the high boiling solvent *N*,*N*′–dimethylpropyleneurea (DMPU) at 110 °C (Fig. 7.35). Different saturated as well as unsaturated fatty acids of different chain lengths were successfully converted into their corresponding alkenes, including lauric, palmitic, behenic and elaidic acid (i.e. C_{12}, C_{16}, C_{22} and *trans*-$C_{18:1}$ carboxylic acids). Yields for the desired 1-alkenes are moderate to good, ranging from 59 to 78% at high catalyst loadings of 3 mol% Pd-precursor and 9 mol% ligand. The α-selectivity is high at these low reaction

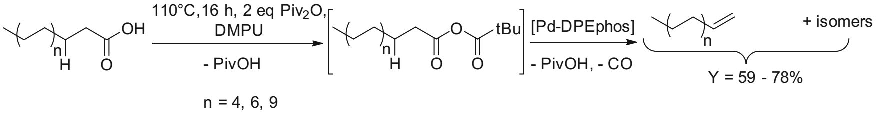


Fig. 7.35 Catalytic decarbonylative dehydration reaction of saturated fatty acids

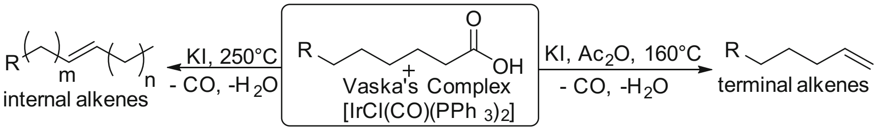


Fig. 7.36 Iridium-catalysed decarbonylative dehydration of aliphatic carboxylic acids to internal and terminal alkenes

temperatures, whilst activity for anhydride formation is low. Hence, to favour anhydride formation, two equivalents of pivalic anhydride are needed, which leads to a less atom economic process.

Scott et al. [112] addressed their research in decarbonylative dehydration on the comparably low yields for 1-alkenes in the low temperature protocol developed by Gooßen et al. They intended to use trialkylamines to reduce isomerisation activity and thereby enabling higher yields for 1-alkenes without drop in selectivity at high conversions. With triethylamine (Et_3N), stearic acid was converted into heptadecenes with selectivity for the 1-alkene of 96% after 16 h and equimolar amounts of Et_3N. Pivalic anhydride ($PivO_2$) was substituted by the more readily available acetic anhydride with comparable conversions and selectivities. In acetonitrile (MeCN) as solvent, a bis(acetonitrile)palladium(II) complex is formed, serving also as an isomerisation catalyst. Hence, the selectivity towards 2-heptadecene from decarbonylative dehydration of stearic acid in MeCN is 59%.

The only example of an iridium catalyst system for the decarbonylative dehydration of fatty acids was presented by Fukuyama and Ryu in 2011 [113]. They applied Vaska's complex $[IrCl(CO)(TPP)_2]$ and were able to switch between the selective formation of either 1-alkenes or mixtures of internal alkenes by varying the reaction conditions and additives (Fig. 7.36).

Two different protocols have been developed, with the main difference being the reaction temperature. At a relatively low reaction temperature of 160 °C, essential anhydride formation has to be promoted by the addition of acetic anhydride, lowering the atom economy of this protocol. However, selectivities for α-olefins are as high as 96–98%. With increasing temperature, anhydride formation proceeds without the addition of promoting anhydrides. At a temperature of 250 °C, isomerisation activity increases, yielding internal alkenes with selectivities >98%. Different saturated fatty acids, e.g. myristic, pentadecylenic, palmitic, margaric, stearic, arachidic and behenic acid, were successfully converted into their corresponding alkenes with yields of 90–94%. Double bonds were almost evenly distributed along the alkyl chain of the resulting olefins. Potassium iodide had to be added in both protocols, presumably for ligand exchange of chloride with iodide.

A very similar protocol has been recently reported by Hapiot et al. for the iridium-catalysed decarbonylative dehydrogenation of unsaturated fatty compounds, such as oleic acid, linoleic acid, ricinoleic acid and undecenoic acid, giving rise to multiple unsaturated linear olefins with triphenylphosphine as ligand [114].

The same group also reported the iron-catalysed decarbonylation/dehydration of different saturated fatty acids. Since iron is very inexpensive and environmentally benign, the high catalyst loadings of 10 mol% $FeCl_2$ still represent a highly attractive protocol for the formation of 1-alkenes. Potassium iodide and acetic anhydride serve as promoters, and with a temperature of 240 °C and 20 mol% of DPPPent (1,5-bis(diphenylphosphino)pentane) the yield for heptadecenes form stearic acid after 3 h is 74% (97/3 ratio of terminal to internal isomers). The reactions has to be conducted under a pressure of CO (20 atm) to assure iron–carbonyl complex formation. Fatty acids of different chain length from C_{14} to C_{22} could be converted to their corresponding alkenes with comparable yields and identical isomer distribution [115].

In 2012, Hillmyer and Tolman [116] modified the protocol for the palladium-catalysed decarbonylation/dehydration initially developed by Miller et al. They aimed for a green and sustainable method for the production of bio-based alkyl acrylates and styrene, from mono-alkyl succinates and hydrocinnamic acid, respectively (Fig. 7.37). The former (i.e. mono-alkyl succinate) is formed by heating the desired alcohol with succinic anhydride, a bio-renewable resource produced from the fermentation of sugars [117, 118]. Hydrocinnamic acid (phenylpropanoic acid) is, e.g. accessible enzymatically from l-phenylalanine [119]. The modified protocol comprises of an increased catalyst loading of 0.25 mol% palladium precursor, 2.2 mol% ligand and one equivalent of pivalic anhydride for the preparation of alkyl acrylates. For example, at a temperature of 190 °C methyl acrylate is produced with 64% yield after 2 h with $PdCl_2$ and TPP as ligand under a flow of nitrogen. By switching the ligand from TPP to Xanthphos and increasing ligand loading to 4.4 mol%, hydrocinnamic acid is converted to styrene in up to 87% yield under otherwise identical reaction conditions. In both cases, immediate distillation of the product form the reaction mixture into a cooled receiving flask is performed [116].

Later on, the same group reported a protocol in which the decabonylative dehydration is performed with preformed *p*-nitrophenylesters in the absence of phospine ligands. For the renewable undecenoic acid, this protocol gives 32% yield of a mixture of different decadiene derivatives [120].

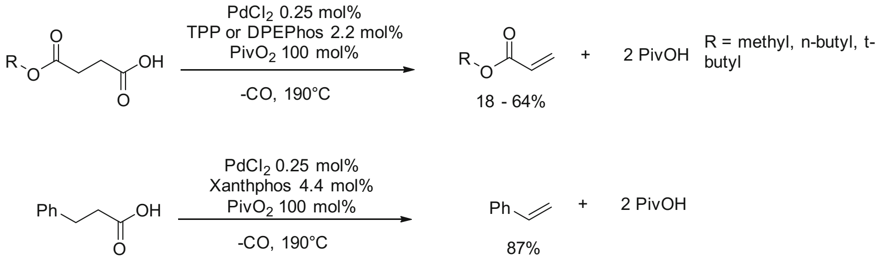


Fig. 7.37 Decarbonylative dehydrogenation of renewable mono-alkyl succinates and hydrocinnamic acid

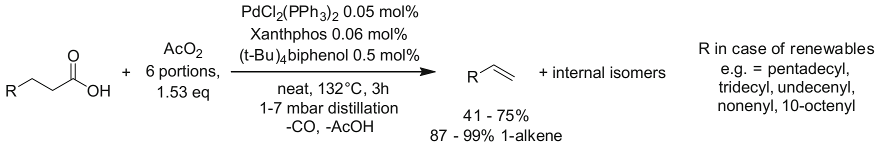


Fig. 7.38 Grubbs' protocol for decarbonylative dehydrogenation of saturated fatty acids

Grubbs, Stoltz and co-workers [121] developed a method for the production of 1-alkenes with palladium systems, combining the advantageous low catalyst loadings of Miller [108] and Kraus [110] and the low temperature of the protocol developed by Gooßen [111] and Scott [112]. Grubbs' improved protocol omits the need for the continuous in situ distillation of the olefin product from the reaction mixture. Additionally, no solvents, basic promoters or expensive pivalic anhydride is used (Fig. 7.38).

Their modifications exhibit the use of Xanthphos as the ligand and the identification of weak acids to enhance overall yield, when using free carboxylic acids rather than preformed anhydrides. Portionwise addition of the promoting acetic anhydride and in situ distillation of the resulting acetic acid at low pressures ensures a consistent acidic level in the reaction mixture affording high α-selectivities. In a typical procedure, they were able to convert stearic acid into heptadecenes with 68% yield and 89% α-selectivity after 3 h at 132 °C and adding 1.53 equivalents of acetic anhydride in six portions every half an hour. This protocol was readily scaled up to convert stearic acid on a 100 mmol scale with maintained yields but slightly higher α-olefin selectivity of 92%.

Aliphatics from oleochemicals are also accessible via catalytic dehydrogenation of fatty alcohols to the corresponding aldehydes with subsequent decarbonylation of the latter. Olsen and Madsen developed a protocol using an iridium-based catalyst for the dehydrogenation/decarbonylation tandem catalysis applied to several benzylic as well as aliphatic alcohols [105, 122]. In the resulting syngas atmosphere, hydrogenation reactions are likely. That means, if the unsaturated oleyl alcohol is used, the corresponding alkane (heptadecane) is formed in approximately 2:1 mixture with unsaturated decarbonylation products, in which the double bond was isomerised (Fig. 7.39). The authors proved the two reactions steps (dehydrogenation and decarbonylation) to operate independently, by observing the accumulation of the intermediate aldehyde in up to 30% with 2-naphtylmethanol as the model substance.

7.4.2 *Glycerol Degradation*

Schlaf et al. intended to develop a new and selective protocol for the production of 1,3-propanediol from glycerol, the co-product of fatty acid derivative production [123]. They wanted to combine acid-catalysed dehydration with

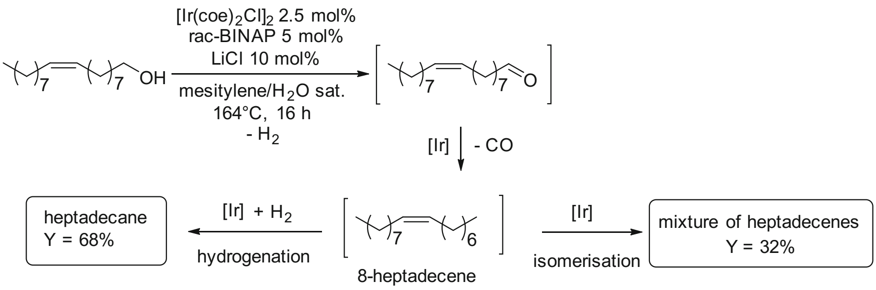


Fig. 7.39 Dehydrogenation/decarbonylation/hydrogenation sequence of oleyl alcohol

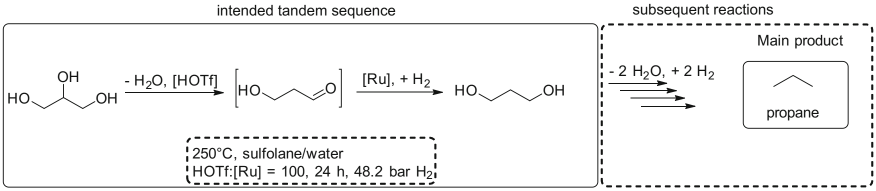


Fig. 7.40 Intended reaction from glycerol to 1,3-propanediol and subsequent reactions

ruthenium-catalysed hydrogenation to yield a selective, orthogonal tandem catalytic system. Triflic acid (HOTf) serves as a dehydration agent, yielding 3-hydroxy propanal, which in principle can be hydrogenated to yield the desired 1,3-propanediol. Different ruthenium aqua complexes were investigated towards carbonyl hydrogenation using model substances under the required harsh, acidic conditions. These homogeneous complexes showed to be stable at temperatures up to 250 °C.

When the developed protocol finally was applied to glycerol in either sulfolane or water, or mixtures thereof, the authors unfortunately were not able to terminate the reaction at the stage of the desired 1,3-propanediol (Fig. 7.40). They ended up with a mixture of products derived from several subsequent dehydration and hydrogenation reactions, with propane being the dead end. Under optimised conditions (250 °C, HOTf : [Ru] = 100, 24 h, 48.2 bar H_2), glycerol was almost completely deoxygenated to propane.

7.5 Isomerising Tandem Catalyses

Isomerising double bonds in order to selectively functionalise the latter is a very promising tool to yield tailored molecules with, e.g. bifunctionalities from readily available unsaturated starting materials [124]. The migration of double bonds can generally be induced thermally or is catalysed by transition metal hydride species by enabling β-hydride elimination. In this regard, terpenes, oleochemicals and phenylpropanoids are very promising starting materials since they can be unsaturated, are usually inexpensive and carry additional functionalities. With the developed tandem catalytic protocols presented in this chapter, these renewable substrates are selectively converted into various products, which are not easy to access via classic organic synthesis.

The developed systems can be subdivided into three main concepts for isomerising double bonds, that is:

- Moving the C=C double bond towards the end of an alkyl chain in order to selectively introduce functionalities in the terminal position;
- Migration of the double bond towards another functionality already present in the starting material, or even in conjugation with, e.g. ester or aromatic moieties to perform, e.g. Michael additions; and
- Unselective isomerisation to yield distributions of isomers after which further reactions yield classes of compounds with different molecular weights.

In the following, different tandem catalytic systems will be presented, with which the authors aim at a selective transformation of the double bond at another position than originally present in the substrate.

7.5.1 Isomerising Metathesis

Isomerisation of double bonds is a typical side reaction observed during homogeneous metathesis reactions and is in most applications undesired. Out of necessity, to make a virtue, isomerisation can be also quite advantageous, e.g. in refining plant oils. Different concepts for the production of olefin blends with shorter carbon chains from unsaturated fatty esters have been developed.

A very early example from 1994 was presented by Grubbs and co-workers [125]. They presented a silver-activated iridium system which is active in both isomerisation and metathesis. Iridium is believed to be the active metal for isomerising metathesis, being an example for auto-tandem catalysis. 1-Octadecene was used as a model substrate, whereas later on the substrate scope was expanded to methyl oleate, showing the functional group tolerance. Catalyst loadings are quite high with 4 mol% $[Ir(coe)_2Cl_2]$ and an excess of AgO_2CCF_3 of 20 mol%, whereas temperature of 85 °C is mild.

The system yields three different molecular classes from methyl oleate, proving the isomerisation to take place before metathesis:

- C_9 to C_{26} linear alkenes
- C_8 to C_{28} linear unsaturated methyl esters
- C_{11} to C_{26} linear unsaturated dimethyl diesters.

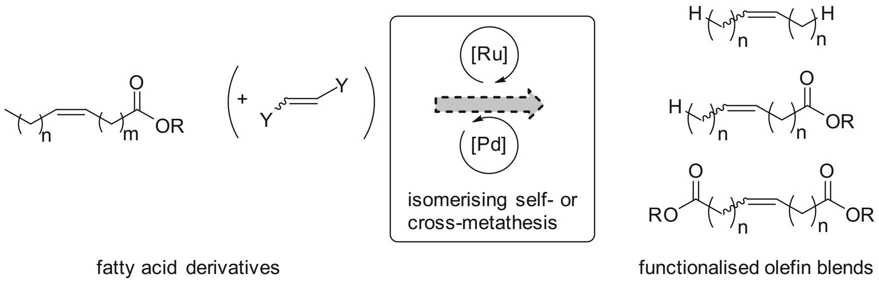


Fig. 7.41 Isomerising metathesis of unsaturated fatty esters with a ruthenium/palladium orthogonal tandem catalytic system

A very similar approach for the refining of oleo chemicals was reported by Ohlmann and co-workers. In 2012, they took advantage of the tremendous development of tolerant Ru-based metathesis catalysts and combined it with a Pd(I) catalyst known to isomerise double bonds with high activity even at low temperature. Isomerising self- and cross-metathesis of fatty acids/esters by using an orthogonal catalyst system comprising of a Grubbs–Hoyveda ruthenium carbene catalyst and $[Pd(\mu\text{-Br})^tBu_3P]_2$ gives complex functionalised olefin blends [126] (Fig. 7.41).

For example, ethene and methyl acrylate were used as co-substrates in cross-metathesis with conversions up to 98%. Valuable diacids/esters and olefins with distinct distributions for the chain length are accessible and can be controlled by the ratio of Ru to Pd and the co-substrate. Cross-metathesis products with ethene can easily be converted to polymers by radical click chemistry, e.g. with dithiols [127, 128], whereas products form cross-metathesis with hexenedioic acid are interesting polymer precursors.

The same orthogonal tandem catalytic system for isomerising metathesis was introduced to the ethenolysis of different phenylpropanoids. Eugenol, safrol, estragol and methyleugenol were converted into their corresponding styrene derivatives. This is an example for the isomerisation of double bonds into conjugation, where the consecutive reaction takes place very selectively. For example eugenol, an extract from clove oil, is converted into the corresponding styrene intermediate via this tandem catalysis under mild conditions, which potentially is interesting for polymer synthesis (Fig. 7.42) [129].

Another application of this useful tool for the selective shortening of unsaturated side chains of phenolic compounds was presented by Goossen in cooperation with Cole-Hamilton [130]. They used an extract of the cashew nut shell liquid (CSNL), a non-edible, low-value by-product of the cashew nut processing, for the synthesis of tsetse fly attractants (Kairomones **A** and **B**, Fig. 7.43).

Key step in the synthesis of a mixture of these kairomones is the isomerising ethenolysis of the key intermediate 3-(non-8-enyl)phenol. This key intermediate is accessible from the CNSL via isolation of anacardic acids, followed by ethenolysis to give a single, terminal unsaturated side chain and final decarboxylation of the

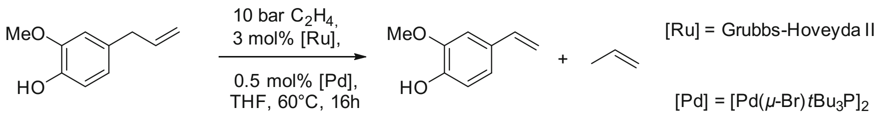
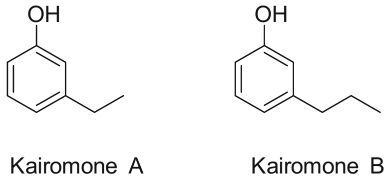


Fig. 7.42 Isomerising ethenolysis of eugenol

Fig. 7.43 Tsetse fly attractants



carboxylic acid moiety. Afterwards, the isomerising ethenolysis of 3-(non-8-enyl) phenol is performed with the known isomerisation Pd(I)-catalyst ($[\mathrm{Pd}(\mu\text{-Br})^t\mathrm{Bu}_3\mathrm{P}]_2$) and the Hoveyda-type NHC catalyst, to give a mixture of 3-ethenyl- and 3-propenylarene. The hydrogenation activity of Ru-metathesis catalysts upon exchanging the atmosphere to hydrogen was used to hydrogenate the double bonds of the side chain to afford the desired mixture (**A**/**B** = 1:1.3) of kairomones in 85% overall yield from 3-(non-8-enyl)phenol (Fig. 7.44). This is an example in which for the first time the hydrogenation activity of metathesis catalysts is used for the hydrogenation of conjugated double bonds derived from isomerising metathesis, representing an *orthogonal*, as well as an *assisted* tandem catalytic systems in synergy.

7.5.2 Isomerising Hydroformylation

Isomerisation of internal double bonds of fatty compounds during hydroformylation reactions is frequently observed as a side reaction leading to mixtures of isomeric aldehydes as the final products [47, 131–134]. However, if a selective isomerisation into the terminal position would be possible, linear aldehydes are accessible. This is highly desirable [134] as linear aldehydes can be transformed into more valuable products, e.g. by hydrogenation to the corresponding linear ester alcohol, a possible polymer precursor.

The isomerising hydroformylation of ethyl oleate to yield the linear aldehyde was presented by Behr et al. [135, 136]. Selectivity towards the *n*-aldehyde is up to 40% at conversions of around 60%, whereas ethyl stearate is the main side product, derived from hydrogenation of the starting material. The product is a high-potential intermediate in polymer applications. An auto-tandem catalytic system comprised of a rhodium precursor in combination with the chelating biphosphite ligand Biphephos is applied. In order to enhance the isomerisation activity and thereby

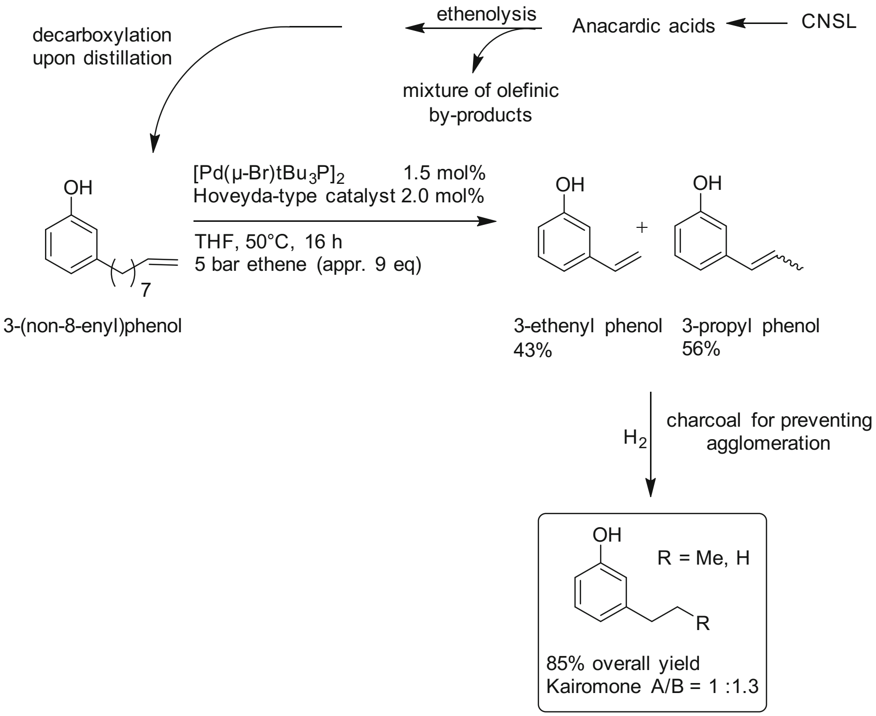


Fig. 7.44 Isomerising ethenolysis and hydrogenation in tandem catalysis as the key steps in the synthesis of tsetse fly attractants from renewable cashew nut shell liquid (CNSL)

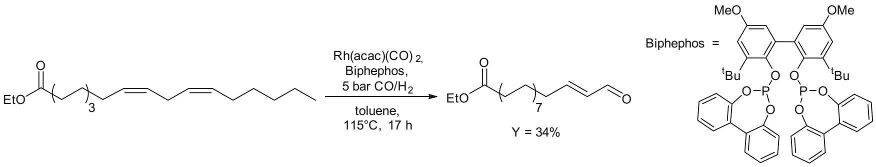


Fig. 7.45 Isomerising hydroformylation of linoleic ethyl ester

providing higher amounts of terminal double bonds, linoleic ethyl ester was applied. Indeed, the in situ formation of a conjugated double bond system at low syngas pressure allowed for the production of the linear aldehyde in 34% yield (Fig. 7.45).

The same catalytic system was applied to the hydroformylation of derivatives of 10-undecenoic acid, the pyrolysis product of castor oil-derived ricinoleic acid. Although these derivatives already carry a terminal double bond, Ternel et al. revealed that inevitably in situ formed internal olefins can also be transformed to the linear aldehyde by isomerising hydroformylation (Fig. 7.46). They based their studies in the isomerising hydroformylation upon undecene nitrile, which they used

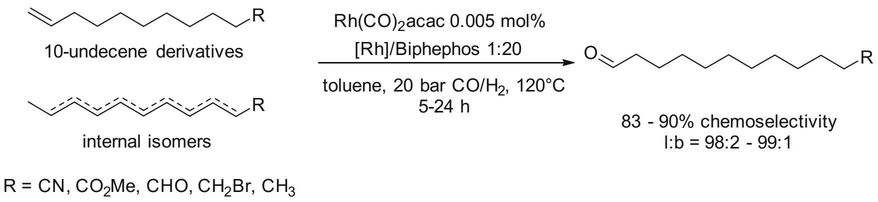


Fig. 7.46 Hydroformylation of 10-undecylenic derivatives including isomerising hydroformylation of internal isomers

in a standard mixture of 95% terminal to 5% internal double bond isomers. They were also able to selectively convert methyl 10-undecenoate, 10-undecenal and 1-bromo-10-undecene, all of them accessible from renewable ricinoleic acid. For methyl 10-undecenoate, full conversion after 24 h with yields for the linear aldehyde of 82% at a linear-to-branched ratio of 99:1 were achieved. For isomerising hydroformylation of undecene nitrile, a recycling of the catalyst by simple solvent and product evaporation under reduced pressure and inert atmosphere was realised. The catalyst remained active for at least five recycling runs at a low concentration of 0.002 mol% rhodium. An additional charge of Biphephos had to be added for each run to preserve high regio and chemoselectivities. The isolated, pure aldehyde is oxidised to the corresponding carboxylic acid by simply stirring in air for 48 h, giving rise to a linear ω-nitrile acid, a potential polymer precursor [137].

Recently, the same group reported that analogous iridium/Biphephos catalytic systems are also capable of performing the hydroformylation/isomerisation reaction very selectively and are only about 5 times less active [138].

A very sophisticated tandem catalytic system based on rhodium and ruthenium was developed by Nozaki et al. in the tandem sequence of isomerisation, hydroformylation and hydrogenation to yield *n*-alcohols from internal alkenes [139]. The key to success is the use of a Rh/biphosphite system for hydroformylation and Shvo's catalyst for hydrogenation of the aldehyde moiety. Applied to methyl oleate, it is possible to yield 53% of the α,ω-alcohol ester with the alcohol functionality in the terminal position (Fig. 7.47). The *n/iso* ratio is remarkably high with 4.4, although hydrogenation of the starting material is the major competing side reaction (yield for methyl stearate 29%). In this special case, where the double bond is buried deep in the alkyl chain, the addition of Ru_3CO_{12} is beneficial in terms of enhanced isomerisation activity.

7.5.3 Isomerising Hydroboration

Another approach towards ω-functionalisation of fatty compounds via selectively isomerising the internal double bond to the end of the alkyl chain was reported by Angelici and co-workers in 2006. Their developed iridium/diphosphine catalyst

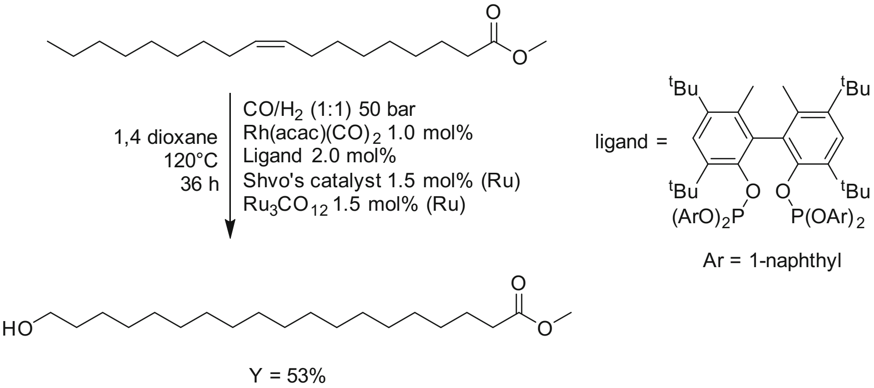


Fig. 7.47 Tandem catalysis of isomerisation, hydroformylation and hydrogenation of methyl oleate

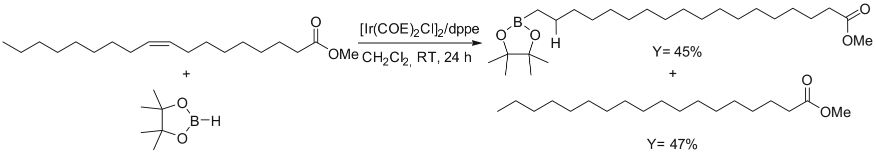


Fig. 7.48 Isomerising hydroboryation of methyl oleate with pinacolborane

system for isomerising hydroboration with pinacolborane represents an auto-tandem catalytic system. At room temperature after 24 h, a catalyst derived from the precursor $[Ir(COD)_2Cl]_2$ and the bidental ligand dppe in dichloromethane yield the desired terminal boronate ester in 45% besides 47% methyl stearate (Fig. 7.48) [140]. The substantial amount of hydrogenation product formed is attributed to the hydrolysis of branched boronate esters that potentially occur during the reaction sequence. Presumably, the α,β-unsaturated fatty ester, which has been identified by NMR studies, is most likely responsible for the reduction.

The terminal boronate ester formed in this reaction sequence is a highly active intermediate in many transformations generally known for boronate esters. Hence, numerous additional terminal functionalised fatty esters are accessible via this intermediate.

Later on, it has also been shown that non-catalytic hydroboration of unsaturated fatty acid derivatives with subsequent thermally induced isomerisation of the organoboron intermediates can also lead to α,ω-bifunctional compounds [141]. Oxidative work-up gives rise to alcohols, but the protocol generally suffers from low selectivity towards one product (e.g. <16% yield for linear α,ω-diol from oleyl alcohol and BH_3*THF) and is non-catalytic. Hence, it will not be further discussed.

7.5.4 Isomerising Trialkylsilylation

An example for ω-functionalisation of fatty compounds was presented by Riepl et al. They developed an auto-tandem catalytic system also based on iridium as catalytically active transition metal for the isomerising dehydrogenative trialkylsilylation of methyl oleate yielding the corresponding terminal vinylsilane (Fig. 7.49) [142].

Norbornene has to be used as sacrificial olefin for capturing in situ formed hydrogen from dehydrogenative silylation. Unfortunately, the authors did not present a detailed investigation of the tandem catalytic system and gave no hint into the direction of potential application of that specific vinylsilane.

7.5.5 Isomerising Lactonisation

Whereas linear bifunctional molecules are accessible via isomerisation of the double bond of oleo compounds to the terminal position, the migration of the double bond towards the carboxylic end also occurs to substantial extent, with the α,β-unsaturated ester being the most thermodynamically favoured. The resulting α,β-unsaturated esters also allow for selective reactions, as shown in the following examples, giving rise to a broad range of natural derived intermediates for various possible applications.

Aliphatic γ-lactones have important industrial applications as, e.g. flavours or food additives. For long alkyl chains, their preparation is most sustainably performed using unsaturated fatty acids. Usually, highly acidic conditions are required, and poor yields, harsh reaction conditions and low selectivity (γ vs. δ-lactone) are achieved. Two very promising approaches towards the tandem catalytic formation of γ-lactones from unsaturated fatty acids are presented in the following.

Gooßen et al. reported on the isomerising lactonisation of unsaturated fatty acids, forming five-ring lactones in one auto-tandem catalytic reactions sequence consisting of isomerisation of the double bond and subsequent in situ 5-exo-trig cyclisation of the acid functionality. They examined this tandem reaction using 10-undecylenic acid and revealed that silver triflate (AgOTf) in chlorobenzene (PhCl) gave the best results in terms of yield for the five-ring lactone. They extended the developed protocol to other commercial mono-unsaturated fatty acids, such as palmitoleic, *cis*-5-dodecenoic and oleic acid and were able to isolate the

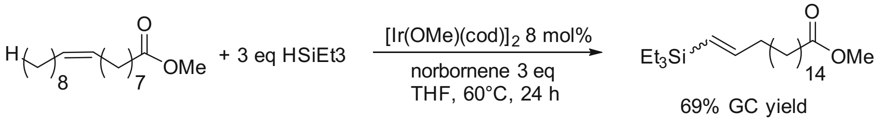


Fig. 7.49 Isomerising trialkylsilylation of methyl oleate to yield the terminal vinylsilane

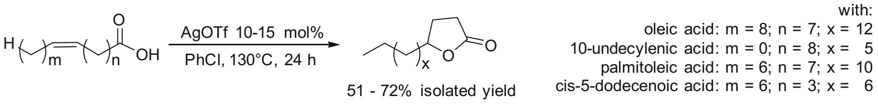


Fig. 7.50 Silver triflate catalysed isomerising lactonisation of fatty acids to corresponding five-ring lactones

corresponding five-ring lactones in 51–71% yields with 10–15 mol% catalyst in refluxing PhCl after 24 h [143] (Fig. 7.50).

The reaction could be up-scaled, and the γ-lactone (γ-stearolactone) of oleic acid was recovered on a 180 g scale to assess the potential chemistry in succession of this intermediate. For example, aqueous saponification using KOH gave the corresponding γ-hydroxy acid in 97% yield. Other ring-opened products with the hydroxyl group in γ-position are obtained upon treatment with n-butanol to the butyl ester (69% yield) and with ethanolamine to the corresponding amide bearing two alcohol functionalities (71% yield).

Kanjilal and co-workers presented a very similar approach to five-ring lactones from unsaturated fatty acids using an ionic liquid derived from choline chloride/$ZnCl_2$ serving as the reaction medium and the auto-tandem catalytic system at the same time [144]. 10-undecylenic acid, oleic acid and erucic acid were converted into the corresponding γ-lactones as the major products. A simple recycling of the catalytic active ionic liquid showed less activity in the second run towards the desired product, in the isomerising lactonisation of 10-undecylenic acid.

7.5.6 Isomerising Michael-Reactions

The most thermodynamically favoured isomer of all possible double bond isomers of fatty acid derivatives is the α,β-unsaturated ester. GOOßEN and co-workers presented two very interesting addition reactions to the β-position of fatty acids by isomerising Michael additions, wherein the double bond has been moved towards the ester functionality [145].

The auto-tandem catalytic system consisting of a rhodium precursor and the diphosphite ligand Biphephos has been investigated in both reactions independently, before merging isomerisation and β-addition (Fig. 7.51).

Selective arylation is achieved with the corresponding tetraarylborate as arylation agent, furnishing the corresponding β-phenyl ester in 30% isolated yield from ethyl oleate. Other short chained unsaturated carboxylic esters showed much higher activity. Esters bearing a tertiary amine in β-position are also accessible via with tandem catalytic pathway (i.e. aza-Michael reaction). For example, pyrrolidine can be introduced to the in situ formed conjugated ester in the β-position with only very little alteration of the reaction conditions. The isolated yields for the corresponding amino esters are 25% when applied to ethyl 10-undecenoate and 17% in the case of

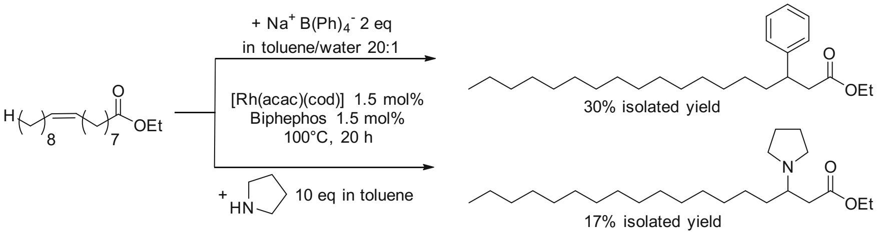


Fig. 7.51 Isomerisation/*β*-functionalisation of ethyl oleate in tandem catalysis

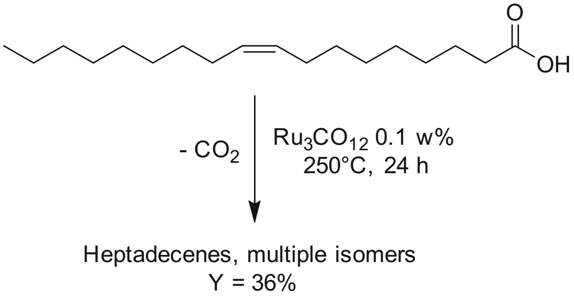
ethyl oleate. The Michael reaction in general is not limited to aminations and arylations, hence representing a flexible tool for β-functionalisations of fatty esters.

7.5.7 Isomerising Decarboxylation

The isomerisation of the double bonds in oleo compounds to the carboxylic end of the chain not only allows for the selective formation of new functionalities or linkages, but also is beneficial in decarboxylation processes for the preparation of alkenes from renewables, like oleic or 10-undecenoic acid (Fig. 7.52). Doll et al. developed a protocol for the formation of the corresponding alkenes from different unsaturated acids, using either triruthenium dodecacarbonyl or $[Ru(CO)_2(EtCO_2)]_n$ as catalyst precursor [146].

The comparison of the activity of the employed catalyst system in the decarboxylation of stearic acid and oleic acid revealed a dramatic increase in the conversion of the acid after 4 h, when the substrate is unsaturated. This proves that isomerisation is needed in order to obtain higher conversions. 10-undecenoic acid could be converted with 0.89 w% catalyst under otherwise identical reaction conditions to 60% to a mixture of the corresponding decenes.

Fig. 7.52 Isomerising decarboxylation of oleic acid



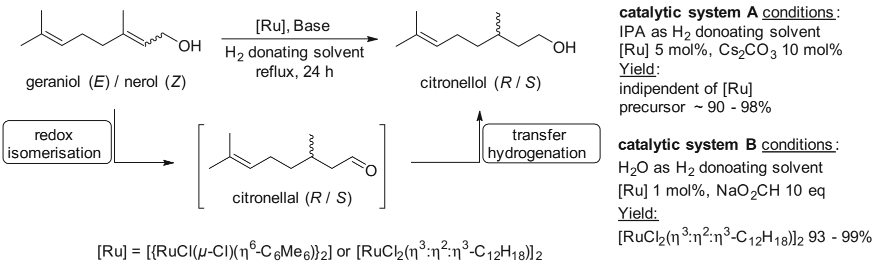
7.5.8 Isomerising Transfer Hydrogenation

The concept of isomerisation of double bonds present in renewable substrates can be extended to, e.g. terpenoids incorporating primary alcohol functionalities. Once the double bond is in α,β-position, the corresponding carbonyl moiety emerges as a result of the tautomeric equilibrium. Cadierno and Gimeno present an auto-tandem catalytic system for isomerising transfer hydrogenation of allylic alcohols, wherein the resulting aldehydes/ketones are selectively transfer hydrogenated using a hydrogen-donating solvent and base (Fig. 7.53) [147, 148].

Thorough studies revealed that Ru-based systems are the most active in both the redox isomerisation of allylic alcohols and transfer hydrogenation. They developed two different catalytic systems, one with isopropanol (IPA) being the hydrogen source under influence of Cs_2CO_3, and the other in water as solvent with excess sodium formate (NaO_2CH). As challenging substrates, they tested their developed protocol on the two renewable substrates geraniol and nerol. The reaction proceeded exceptionally selective for isomerising transfer hydrogenation of allylic alcohols to yield citronellol from both substrates. The other double bond is not affected at all, representing very high chemoselectivity. In refluxing IPA, both ruthenium precursors are almost equally active, giving yields of citronellol with 5 mol% [Ru] of 90–98% after 24 h. In refluxing water and excess sodium formate, the precursor $[RuCl_2(\eta^3{:}\eta^2{:}\eta^3\text{–}C_{12}H_{18})]_2$ is most active, yielding 93–99% citronellol after 24 h at a low concentration of 1 mol%. ($C_{12}H_{18}$ = dodeca-2,6,10-triene-1,12-diyl).

7.5.9 Isomerising Alkoxycarbonylations

One of the most investigated and highly selective possibilitie to introduce functionalities in the ω-position of the carbon chain of unsaturated fatty acid methyl esters are isomerising alkoxycarbonylations. These palladium-catalysed reactions yield esters from carbon monoxide, olefins and an alcohol. By tuning the electronic environment of the palladium catalyst, the reaction is very selective to terminal



catalytic system A conditions:
IPA as H_2 donoating solvent
[Ru] 5 mol%, Cs_2CO_3 10 mol%
Yield:
indipendent of [Ru]
precursor ~ 90 - 98%

catalytic system B conditions:
H_2O as H_2 donoating solvent
[Ru] 1 mol%, NaO_2CH 10 eq
Yield:
$[RuCl_2(\eta^3{:}\eta^2{:}\eta^3\text{-}C_{12}H_{18})]_2$ 93 - 99%

[Ru] = $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6Me_6)\}_2]$ or $[RuCl_2(\eta^3{:}\eta^2{:}\eta^3\text{-}C_{12}H_{18})]_2$

Fig. 7.53 Isomerising transfer hydrogenation of allylic alcohol moieties in terpenoids

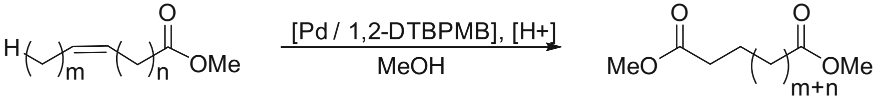


Fig. 7.54 Isomerising methoxycarbonylation of an unsaturated fatty acid methyl ester to yield the linear diester

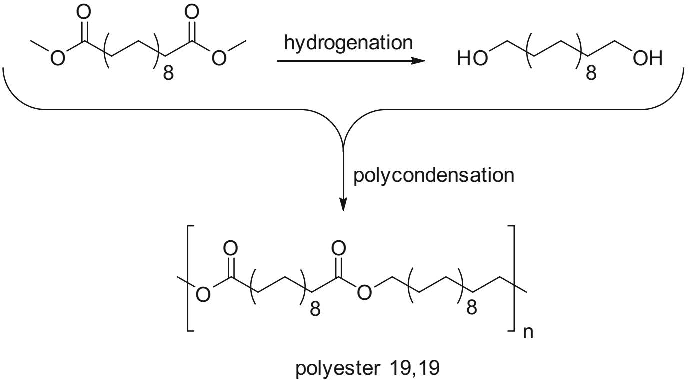
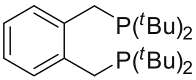


Fig. 7.55 Polycondensation of C19-diester from methoxycarbonylation of methyl oleate with the corresponding diester derived from hydrogenation

double bonds with very high linearities of the resulting ester (Fig. 7.54). As Pd-hydride species are very potent isomerisation catalysts, the careful choice of the employed ligand allows a highly selective isomerising alkoxycarbonylation. Only the terminal double bond isomers selectively react to yield linear, long-chain diesters, potential monomers for polyesters, with properties very similar to those of polyethylene (Fig. 7.55) [149–155].

The auto-tandem catalytic system usually applied for isomerising alkoxycarbonylations was developed in the first place by Eastham et al. for the production of methyl propanoate from ethene, which is an intermediate in the α-process of Lucite [156–159]. It consists of a palladium precursor in combination with the sterically demanding diphosphine ligand 1,2-bis((di–*tert*–butylphosphino)methyl)benzene (1,2-DTBPMB) (Fig. 7.56), with addition of a Brønsted acid. Ongoing work by Jiménez-Rodriquez et al. [160, 161] has revealed that internal alkenes can be converted to linear esters under very similar conditions, representing the first example for isomerising alkoxycarbonylation with this system.

Fig. 7.56 1,2-bis((di-*tert*-butylphosphino)methyl) benzene (1,2-DTBPMB)



The first example of diester synthesis form unsaturated esters (including acrylates and methacrylates) has been also reported by Cole-Hamilton et al. [162]. They were the first to selectively transfer fatty acid methyl esters to the corresponding α,ω–diesters by isomerising methoxycarbonylation. Methyl oleate is reacted with the aforementioned catalyst system [Pd/1,2-DTBPMB] and methanesulphonic acid at 80 °C and 30 bar CO pressure for 22 h to yield dimethyl 1,19–nonadecanedioate with a selectivity for the α,ω-diester of >95%.

Mecking and Quinzler reported for the first time the reduction linear C_{19}-diester derived from methyl oleate to the corresponding diol. The polycondensation of the diester and the diol was conducted, yielding polyester-19,19 for the first time (Fig. 7.55) [149, 150]. The isomerising ethoxycarbonylation of erucic acid to yield C23-diester and subsequent reduction to the corresponding diol was also reported in this paper. Via this pathway, an even longer polyester is accessible (polyester-23,23) from renewable substrates. The properties of these two new polyesters are more similar to these of polyethylene in comparison with currently accessible long-chain linear polyesters (poly(decamethylene sebacate)).

After these two major findings (i.e. development of the auto-tandem catalytic system capable of promoting the isomerising alkoxycarbonylation of fatty acid methyl esters, and the potential application of the resulting product in polycondensates), much effort has been directed towards improvement, extension and scale-up of this reaction.

Applying “high oleic sunflower oil” (HOSO) as the starting material for isomerising methoxycarbonylation, Köckritz et al. were able to yield the desired C_{19}-diester in 97% yield under optimised conditions [163, 164]. The treatment of the employed triglyceride in methanol with the acidic catalyst system required for methoxycarbonylation leads to a transesterification giving rise to glycerol and mainly methyl oleate, which subsequently is reacted to the C_{19}-diester. The authors found that this extended tandem catalytic system is superior to the stepwise synthesis, in terms of overall yield, and can easily be up-scaled to a 12-L tank reactor.

Further studies have been performed directed to the application of the C_{19}-diester as a platform intermediate in renewable monomer production for potential polycondensates. C_{19}-diacid is available via alkaline hydrolysis and the corresponding diol also via catalytic, atom economic hydrogenation using molecular hydrogen and a ruthenium-based system. The latter had been transformed to the C_{19}-diamine by catalytic amination using ammonia (Fig. 7.57). The polycondensation of diamines with the corresponding diacids to novel polyamides has been reported by Stempfle et al. [165].

Additional improvements include the use of natural oils from a local grocery store (olive, rapeseed and sunflower oil) [166], the use of cheaper sulphonic acid instead of methanesulfonic acid plus the extension to additional natural oils (soybean and peanut oil) [167] and the incorporation of tall oil fatty acids (TOFA), a low-value side product of the paper industry. All of the mentioned examples selectively yield the C_{19}-diester from the applied feedstock [168]. Additionally, algae oil was also shown to allow access to diesters via this methodology, giving rise to novel, algae-based polyesters [169].

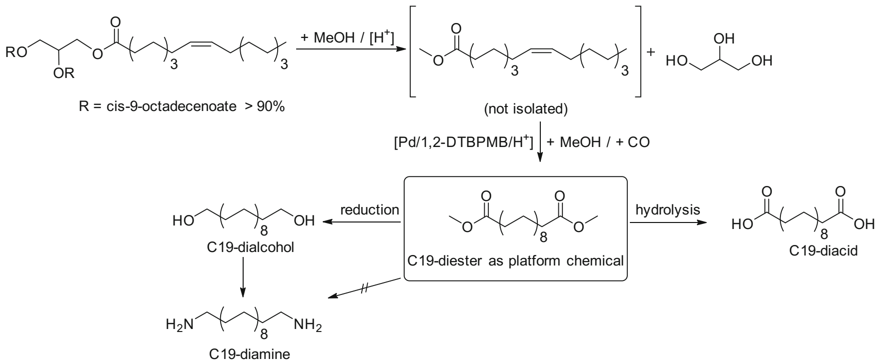


Fig. 7.57 Tandem reaction sequence leading from, e.g. HOSO to dimethyl 1,19–nonadecane-dioate and polymer precursors derived thereof

Even more selective adamantly-analogues to the 1,2-DTBPMB ligand have been presented [170], the mechanism of isomerising methoxycarbonylation was studied in detail [171], and the scope has been extended to different unsymmetrical α,ω-bifunctinoal molecules from oleo chemicals [172].

The recycling of an auto-tandem catalytic system involving Pd(hfacac)$_2$ and XANTphos for the methoxycarbonylation of methyl oleate was investigated by Behr et al. [173]. Thermomorphic solvent systems were applied consisting of methanol and different *n*-alkanes to allow for an easy phase separation after reaction. Unfortunately, the selectivities for the linear C$_{19}$-diester are low ($\sim$19%) compared to systems with 1,2-DTBPMB. Nevertheless, in decane, a successful recycling of the palladium catalyst was realised, with only 2 ppm leaching into the apolar phase. The activity could be remained for at least three recycling runs.

Beller et al. were able to yield the C$_{19}$-diester from methyl oleate applying the same catalytic system as originally developed by Cole-Hamilton et al., substituting toxic carbon monoxide with formates (i.e. HCOOMe). This tuning allows for isomerising alkoxycarbonylation under atmospheric pressure and makes the implementation of this methodology feasible in “normal” glass ware used in organic laboratories rather than high-pressure equipment [174].

Recent work in the group of Mecking at the university of Konstanz/Germany proved that the general protocol of isomerising alkoxycarbonylation can be applied to a much broader range of substrates than only classic oleo chemicals. They were able to transform the renewable terpene citronellic acid into a diester applying the aforementioned catalytic system (Fig. 7.58). Notably, the double bond isomerises from a trisubstituted position to the terminal position. Subsequently, reduction in the diester was performed and the corresponding diol used together with the diester to synthesise a novel, terpene-based polyester.

Recent effort of the work group has been addressed to also allow the synthesis of carboxylic acids in an isomerising manner with the known catalytic system.

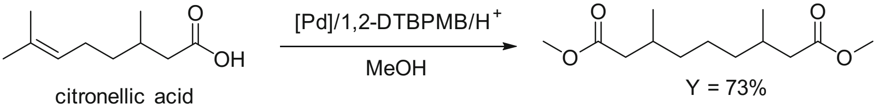


Fig. 7.58 Isomerising alkoxycarbonylation of citronellic acid yielding a diester

Hydroxycarbonylation with water has been presented, and the selectivity to the corresponding 1,19-nonadecandioic acid was >90% with a maximum turnover number of 120 [175].

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Chapter 8
Continuously Operated Telomerisations with Renewables in Miniplants

Arno Behr and Andreas J. Vorholt

Process development of new chemicals always starts in the laboratory in discontinuous, i.e. batch experiments. When all important reaction conditions are checked and sufficient results concerning yield, selectivity, and catalyst activity are obtained, a first economic feasibility study is carried out to clarify whether the new product should be produced commercially. If this study is positive, the scale-up of the product begins. This scale-up can be done in different ways:

Originally, an "**integrated pilot plant**" was constructed with a scale-up factor of about 10^3. When the product is synthesised in the laboratory in amounts of 10–100 g, the continuously operated pilot plant is designed for the production of 10–100 kg/h. Therefore, this plant has to be built with relatively big machines and devices, which must be constructed individually by special equipment manufacturers. This makes the pilots plants relatively expansive, and the construction of the facilities takes a long time—possibly several months or even a year. When the pilot plant is ready, the following operation time is relatively long since big amounts of chemicals must be handled.

The second, more modern possibility in scale-up is the use of "**miniplants**" [1, 2]. In this case, the increase in apparatus size is only low, but again the plant works in a continuous way. The production of the new chemical is done in a scale of 10 g/h to at most 1 kg/h. Using this technique, the miniplant can be constructed with common, purchasable laboratory equipment like steel or glass reactors of dimensions of 0.5–2 L. In addition, pumps, thermostats, cryostats, controllers, valves, or pipes can be easily purchased without a special construction of expensive purpose-built items. The construction time of a miniplant often lasts only 3–4 months. The operation of the miniplant and possible reconstructions can be carried out, easily. Thus, the use of the miniplant technique is relatively cheap and provides quick but accurate results.

In homogeneous catalysis, the great advantage of miniplants is the easy check of the catalyst lifetime in a small scale. Different catalysts can be investigated successively, and the costs of operation are low. In a miniplant, all recycling streams can be closed, and the influence of accumulations on the catalyst can be

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investigated [3–5]. In the laboratory, recycling tests are very time-consuming and often inaccurate because of small catalyst losses or contact with air. The catalyst recycling in a continuously operated and closed miniplant is easily done and very secure. Long-term experiments of about a week or longer are of no problem [6].

In the following chapters, the construction and operation of miniplants will be described on different examples with renewables in which also carbon dioxide will be considered. The telomerisation of 1,3-butadiene with CO_2, glycerol and sucrose will be described in the present Chap. 8. Additionally, the co-oligomerisation of fatty compounds with ethene (Chap. 9), the hydroamination of the terpene myrcene (Chap. 10), and the hydroformylations (Chap. 11) of unsaturated oleochemicals are discussed.

8.1 Telomerisation of Butadiene with Carbon Dioxide

The telomerisation of 1,3-butadiene **1** with carbon dioxide **2** was first discovered by Inoue [7] and Musco [8] (see Chap. 5). The main product of this reaction is the δ-lactone 2-ethylidene-6-hepten-5-olid **3** (Fig. 8.1). Besides this target molecule also the γ-lactone **4,** the carboxylic acid **5,** and the ester **6** are formed. A further side product is the dimerisation product 1,3,7-octatriene **7**.

The optimum catalyst of this reaction is an in situ catalyst formed by the precursor palladium *bis*–(acetylacetonate) and, e.g., the bulky ligand tricyclohexylphosphine. Inspite of the low activity of CO_2, this telomerisation occurs already at very mild reaction conditions, for instance, at 80–90 °C and 10–40 bar. A typical reaction solvent is acetonitrile. In batch experiments, a conversion of butadiene of 48% and a high selectivity to the δ-lactone of 95% could be reached.

Considering these starting conditions, a first miniplant concept was designed (Fig. 8.2): The reaction occurs in a 3 L continuously stirred tank reactor (CSTR) with a residence time of 15 h. The condensed butadiene is pumped from a buffer

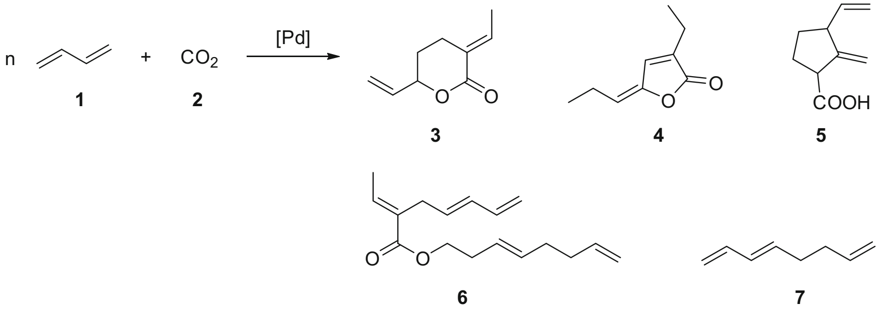

Fig. 8.1 Products of the telomerisation of 1,3-butadiene with carbon dioxide

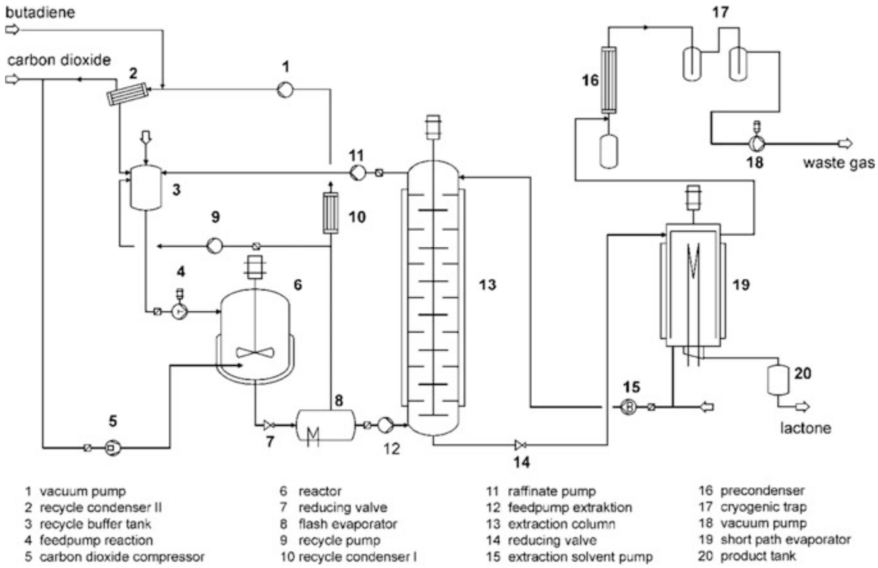

Fig. 8.2 Miniplant I for the telomerisation of 1,3-butadiene with carbon dioxide

tank into the reactor, and the carbon dioxide is pressed in via a compressor. The effluent of the reactor contains 20% of δ-lactone, but also unreacted butadiene, CO_2, acetonitrile, the side products, and the catalyst [9].

This mixture is then separated by flash evaporation in reduced pressure at temperatures below 100 °C yielding a vapour phase with carbon dioxide, butadiene, and acetonitrile (which can be recycled to the reactor) and a liquid phase consisting of more than 95% δ-lactone, side products, and catalyst. At first, a distillation of this product mixture was avoided because it was known that at higher temperatures and longer load periods the δ-lactone **3** converts into the non-wanted γ-lactone **4.** Thus, a smooth extraction step was developed: With 1,2,4-butanetriol, which has a clearly higher boiling point than the δ-lactone, the lactone could be extracted nearly completely from the mixture at a mild temperature of 60 °C. At lower temperatures, the viscosity of the triol is too high. In batch experiments, no additional reaction of the extractant solvent was observed. The raffinate phase of the extractor containing the higher boiling side products, and the catalyst was recycled to the reactor; the catalyst-free extract phase containing the triol, and the δ-lactone was separated by vacuum distillation in a short path evaporator with a short retention time and a heating medium temperature of 145 °C. Thus, a pure δ-lactone was isolated, and the triol was recycled back to the extractor.

These operations were carried out continuously in miniplant I for 24 h run-time. The non-reacted starting compounds, the solvent acetonitrile, the catalyst, and the high boiling side products were recycled continuously. Surprisingly, no accumulation of the side products occurred. Obviously, in the reactor, these side products are in a catalysed equilibrium with the δ-lactone so that no new side products are formed. Thus, in the miniplant I operated continuously for 24 h butadiene, and carbon dioxide seemed to react selectively only to the wanted δ-lactone.

However, in the operation of the miniplant for a running time of several days, a considerable decrease of the yield of the δ-lactone was observed. In addition, it was also realised that small amounts of the extractant 1,2,4-butanetriol occurred in the raffinate stream which accumulated in the reaction phase, thus slowly deactivating the catalyst.

The separation concept had to be changed, and a reconstructed miniplant II had to be installed [10–12]. The flow scheme of the slightly changed miniplant is show in Fig. 8.3.

In miniplant II, the extraction step was removed and instead the already existing short path evaporator was used to separate the catalyst from the product. However, this thermic separation is only possible at temperatures which do not destroy the catalyst. After careful optimisation of the separation conditions, the following steps were developed: The reaction mixture is first separated in the flash evaporator at 80 °C and 150 mbar. The remaining liquid phase, containing δ-lactone, side products, and catalyst, is then conducted to the short path evaporator where the δ-lactone is smoothly separated from the catalytic residue at 80 °C and 1.5 mbar. Using these conditions, miniplant II was operated for several days where the miniplant worked satisfying under steady-state conditions. The miniplant produced the δ-lactone in a constant amount of 8 g/h without catalyst deactivation or side product accumulation. In an industrial production of the δ-lactone, the very high vacuum generates relatively high costs which are only economic if the product is sufficiently valuable.

A certain disadvantage of the hitherto process is the fact that toxic acetonitrile is used as solvent. To avoid this handicap, other solvents were investigated, and it was found that cyclic carbonate solvents like ethylene, propylene, or butylene carbonate

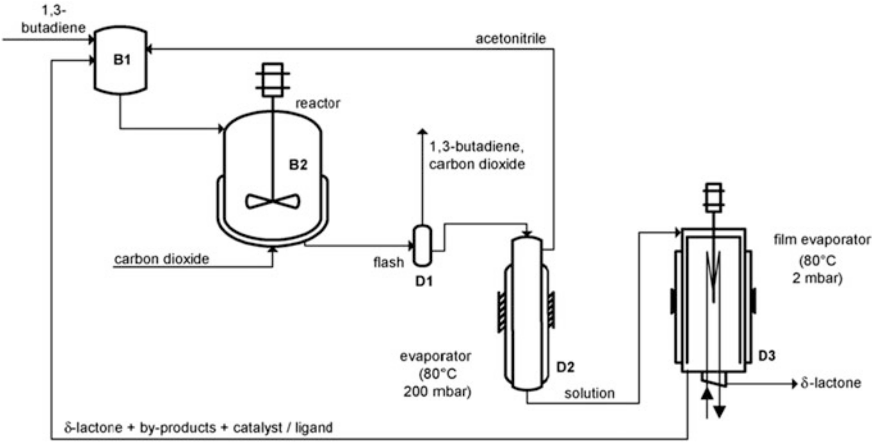

Fig. 8.3 Miniplant II for the telomerisation of 1,3-butadiene with carbon dioxide

are very attractive solvents in CO_2 telomerisation [11, 12]. Furthermore, cyclic carbonates with ester groups like glycerol carbonate propionate or butyrate could be tested successfully. These glycerol carbonates have the advantage that their boiling points are much higher than the boiling point of the δ-lactone. Thus, they are not separated in the flash evaporator but as high boilers in the short path evaporator.

8.2 Telomerisation of Butadiene with Glycerol

The telomerisation of butadiene with the trifunctional molecule glycerol yields a number of different products because in principle all three hydroxy functionalities of the glycerol—both primary and secondary ones—can react in the telomerisation reaction. Thus, unsaturated linear or branched mono-, di- and trioctadienylethers can be formed (Fig. 8.4). Of course also the butadiene-dimer, 1,3,7-octatriene can be formed as unwanted by-product.

Especially, the telomers which still obtain free hydroxy groups are of high industrial significance because they can easily be converted to anionic or non-ionic detergents, emulsifiers, or anti-foaming agents. However, if the telomerisation is carried out in a homogeneous phase, e.g. in isopropanol, only broad mixtures are formed which contain both non-reacted glycerol and a greater amount of the non-wanted tritelomers. Thus, the reaction performs better in an organic-aqueous biphasic system. The palladium catalyst is formed in situ from $Pd(acac)_2$ and the sodium salt of triphenyl-phosphine-trisulfonate (TPPTS). The palladium catalyst dissolves splendidly in the water phase in which also the glycerol is solved. The second phase is an organic phase, e.g. a solvent like toluene or the compressed liquid starting compound butadiene. By extensive mixing, sufficient butadiene solves in the water–glycerol–catalyst phase where the reactions take place. The first reaction step is the formation of the monooctadienylether of glycerol which dissolves relatively well in the organic phase so that no (or little) further reaction to the di- and tritelomers can occur. Thus, the biphasic telomerisation of butadiene with glycerol yields relatively selective the monotelomers and few amounts of the ditelomers. A slight disadvantage is the fact that in the presence of water also small amounts of the water telomer, the 2,7-octadienol, is formed (Fig. 8.5).

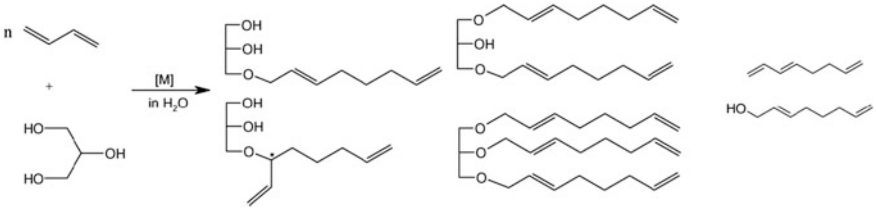

Fig. 8.4 Products of the telomerisation of butadiene with glycerol

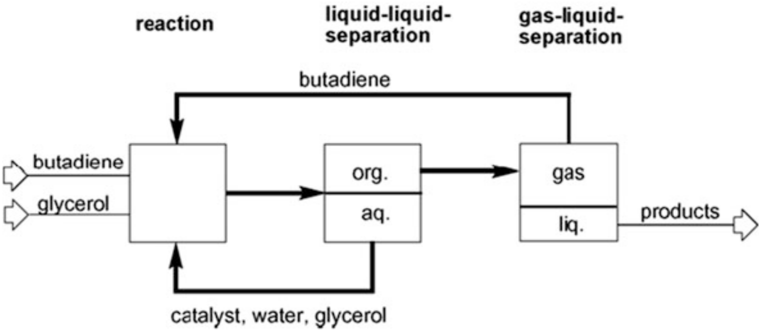

Fig. 8.5 Process scheme of the biphasic telomerisation of butadiene with glycerol

This liquid–liquid two-phase technique, which was already applied successfully in glycol telomerisation [13–16], is also very suitable for glycerol telomerisation [17]. As shown in Fig. 8.5, this technique has the great advantage that by a simple liquid–liquid-separation step the catalyst is separated from the products and can easily be recycled to the reactor. The organic product phase still contains some unreacted butadiene which can also be recycled via a subsequent gas–liquid separation step.

For this telomerisation, a continuously operated miniplant was constructed [18–20] (Fig. 8.6). Due to the application of stabilizing agents, such as phosphonium salts and radical scavengers to prevent the polymerisation fouling of butadiene, this process could be run for more than 250 h with constantly high yield of monotelomers and a low palladium leaching below 20 ppm. All recycling loops were closed, and a space-time yield of 20 kg m^{-3} h^{-1} was obtained.

8.3 Telomerisation of Butadiene with Sucrose

As already mentioned in the telomerisation chapter, the reactions with sugars as nucleophiles are very attractive. Monosaccharides like glucose, xylose, or arabinose were already tested, but also disaccharides like sucrose or even polysaccharides like starch have been used in telomerisation with butadiene or sometimes with isoprene or piperylene [20].

In the glycerol miniplant described above—after some minor modifications—also the telomerisation of butadiene and sucrose was tested in continuous operation [21]. With the same Pd/TPPTS catalyst, the liquid–liquid two-phase technique was used with a mixture of water and isopropanol as polar catalyst phase. A mixture of eight isomeric telomers was formed which proved all to be sucrose monooctadienyl ethers. Once again small amounts of 2,7-octadienol occurred as by-products. In this isopropanol–water mixture, the amount of palladium in the organic product phase was only 11 ppm. A great technical problem during the investigations was the

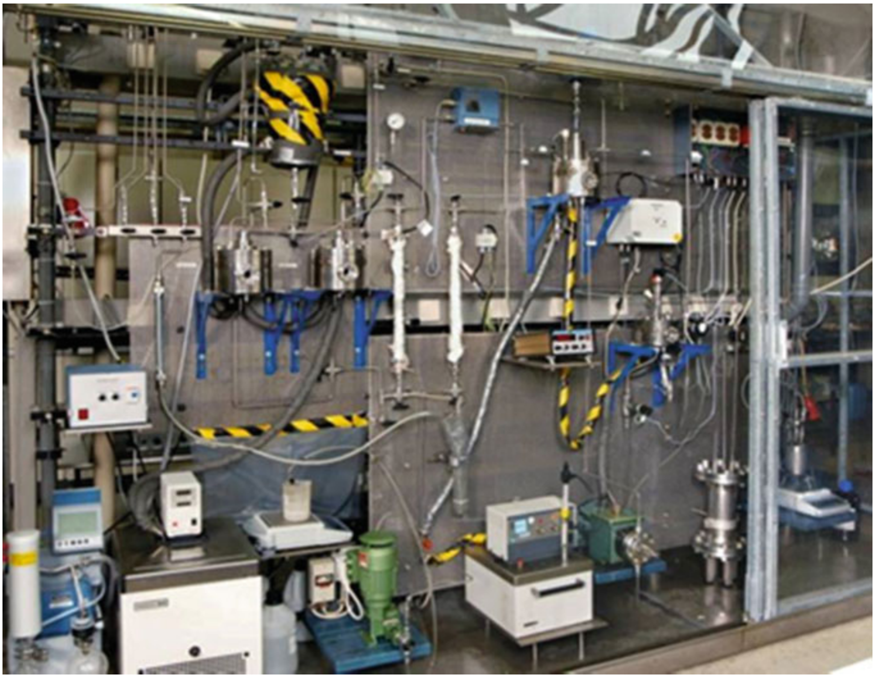

Fig. 8.6 Picture of the continuously operated miniplant for the telomerisation of butadiene with glycerol

dosage of the small amounts of the solid material sugar in the miniplant scale. To circumvent this problem, the nucleophile sucrose was fed into the plant as a highly concentrated aqueous sugar solution. However, using this technique, the water is little by little enriched in the reaction part of the miniplant, thus not allowing a really stationary operation. Like the well-known alkyl polyglucosides (APG), the sucrose monotelomers are of high interest for the detergent market.

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Chapter 9
Continuously Operated Cooligomerisation of Fatty Compounds with Ethylene

J. Hasselberg, Arno Behr and Andreas J. Vorholt

9.1 Introduction

Branched fatty derivatives are particularly used in lubricant industry. Branched fatty derivatives have at least one branching point in the alkyl group resulting in a change of the three-dimensional structure which leads to a molecular angling [1]. Due to this angling of the carbon chain, the branched derivatives can be clearly distinguished from the linear homologs in their physical properties [2–5].

The huge commercial potential, particularly in cosmetics and lubricants industry, is based on the following typical properties of branched fatty derivatives [6, 7]:

- Low melting point
- High thermal and oxidative stability
- Low viscosity
- Low surface tension
- High wettability (spreadability)
- High solubility of the corresponding salts in aqueous and organic solutions
- Low packing density
- High water vapour permeability.

The low melting point allows the application in refrigeration as well as in high temperature technology. Branched fatty derivatives are stable and liquid over a wide temperature range and their low viscosity and surface tension lead to good lubricant properties [7].

The high solubility and wettability result in a higher hydrophilie and give commercial potential in the cosmetics industry. Due to the low packing density caused by the branched carbon chain, the crèmes, lotions, and deodorants have high water vapour permeabilities. Concurrently, the high chemical stability ensures the required colour and odour stability [8, 9]. The high spreadability leads to a low critical micelle concentration, which allows the application as detergents additives, or in the production of surfactants. Because of the high solubility of the corresponding salts, they

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can be additionally used as drying agents for paints and coatings, for the extraction of metals, for corrosion protection, and as additives in polymers.

9.1.1 Cooligomerisation of Fatty Compounds with Ethylene

Branched fatty derivatives are industrially produced as side products of fatty acid dimerisation or "Guerbetisierung" of fatty alcohols [10–12]. Further ways for the synthesis of branched fatty derivatives are described among others from Metzger et al. [13], Foglia et al. [14] and Behr et al. [15].

An alternative process for the production of branched fatty derivatives is the cooligomerisation of diunsaturated fatty compounds such as conjugated linoleic acid or methyl linoleate, which has already been investigated in laboratory scale [16–21].

Within those investigations, the direct formation of the branched derivatives from linoleic acid or methyl linoleate with ethylene was investigated (Fig. 9.1). The reaction scheme shows a tandem reaction consisting of the conjugation of methyl linoleate to methyl conjugate followed by the cooligomerisation of methyl conjugate with ethylene to the branched fatty derivatives.

This route leads directly from industrially easily accessible basic oleochemicals (linoleic acid technical: 62.0 w-% or methyl linoleate technical: 59.3 w-%) to the designated product.

The cooligomerisation was investigated with linoleic acid [21] as well as with methyl linoleate [22] like it is described in the following chapters. The examination of reaction conditions and achieved yields showed no significant differences between the different oleochemical educts.

9.2 Batch Investigations

9.2.1 Conjugation and Cooligomerisation in Laboratory Scale

The tandem reaction consisting of conjugation and cooligomerisation requires a catalyst, which favours both reactions. Within the investigations of the isolated conjugation, highly active as well as moderately active homogenous catalysts could be found [9]. Concerning the tandem reaction, only $RhCl_3 \cdot 3H_2O$ appeared as a promising homogenous precursor. This precursor has already been successfully used for conjugation with ethylene in investigations of Behr and Laufenberg [16], Behr and Fängewisch [19], Behr and Miao [20], and Behr et al. [21].

While the catalyst based on the $RhCl_3 \cdot 3H_2O$ precursor is only moderately active regarding the isolated conjugation, it is highly active for the cooligomerisation so that the chemical equilibrium is shifted in favour of the branched products.

Additionally to the precursor $RhCl_3 \cdot 3H_2O$, in which the active rhodium species has the oxidation state III, a regeneration additive in form of an alkyl halides is

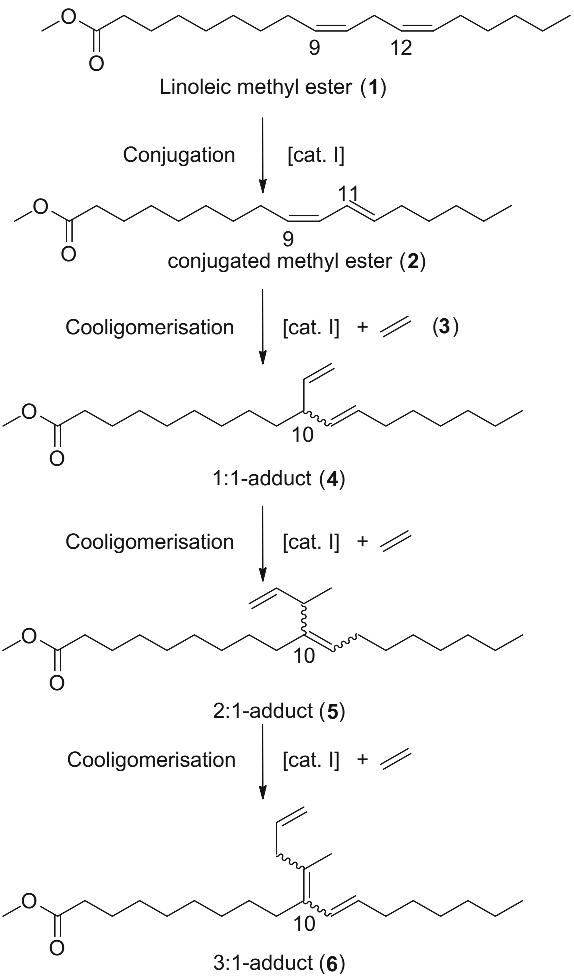


Fig. 9.1 Tandem reaction of methyl linoleate and ethylene forming branched fatty derivatives

needed. The addition of an alkyl halide like crotyl chloride is necessary for the reoxidation of the inactive Rh(I)-species, which appears during the catalyst cycle. At optimised reaction conditions, the achievable yield of branched derivatives via tandem reaction is around 92% (Fig. 9.2). The formation of the product is consecutive: At first the methyl conjugate is formed, secondly one molecule of ethylene is added to form the 1:1 derivative **4**. Before the next molecule of ethylene can be added, a conjugation has to occur once again so that the 2:1 derivative **5** can be formed. Higher branched products than the 3:1 derivate **6** have not been detected.

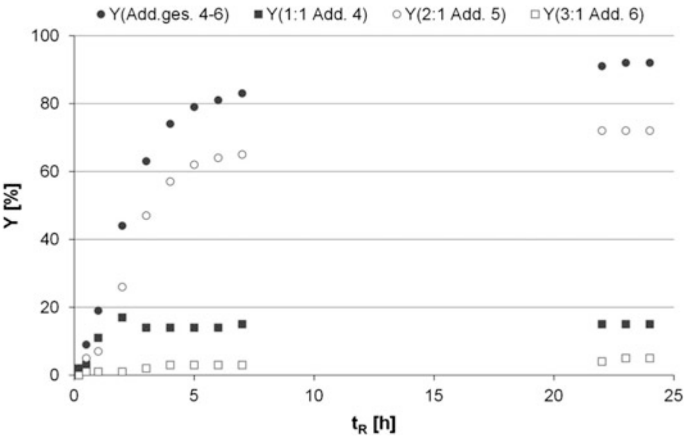


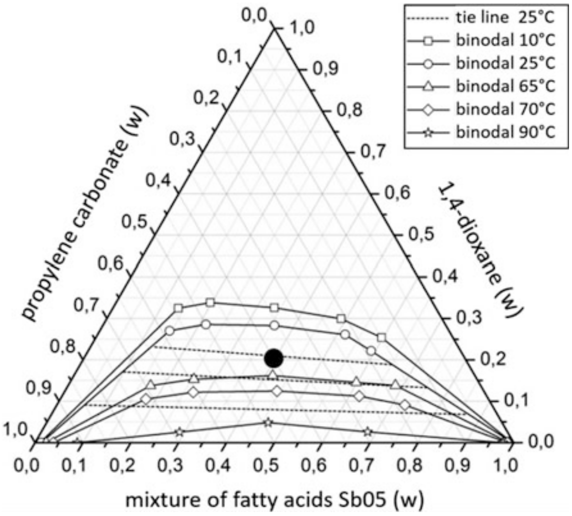
Fig. 9.2 Yield time curve for the production of branched fatty derivatives [21]. Reaction conditions: *Cat.* $RhCl_3 \cdot 3H_2O$; *Reg.* Crotyl chloride; *Solvent* 1,4-Dioxane; *Educt* Emery Edenor SB05 (w-% of linoleic acid in educt $w_{\text{linoleic acid}} = 0.62$); $w_{\text{Emery,SB05}} = 0.4$; $w_{\text{Propylene Carbonate}} = 0.4$; $w_{\text{1,4-Dioxane}} = 0.2$; $c_{\text{cat.}} = 1$ mol%; $n_{\text{Reg}}/n_{\text{Kat}} = 25$; $T_R = 70$ °C; $p_{\text{Ethylene}} = 10$ bar contin.; 750 rpm

9.2.2 Catalyst Recycling

To recycle the catalyst, a thermomorphic multicomponent solvent (TMS) system is used. The TMS consists of the polar component propylene carbonate, the medium polar solvent 1,4-dioxane, and the non-polar fatty compounds. The ternary diagram in Fig. 9.3 illustrates the liquid–liquid equilibrium of this mixture [21].

At room temperature and below the indicated operating point ($w_{\text{propylene carbonate}} = 0.4$, $w_{\text{Emery,SB05}} = 0.4$ and $w_{\text{1,4–dioxane}} = 0.2$) is a two-phase mixture so that

Fig. 9.3 Ternary diagram for propylene carbonate, 1,4-dioxane and fatty compounds (Emery Oleochemicals Edenor SB05) *filled circle* operating point [21]



the catalyst recycling can be easily realised by separation of the liquid phases. At a reaction temperature of 70 °C, the mixture consists of only one liquid phase which is very important to control the considered reaction. In case of a gas–liquid–liquid reaction system, the cooligomerisation is highly limited by mass transfer which is indicated by a critical reduction in yield.

9.2.3 Catalyst Leaching

Using the described TMS-system, the catalyst leaching was higher than it was anticipated. That is why the cause for a high loss of the catalyst into the product phase was investigated, initially.

Propylene carbonate solvated the homogenous rhodium catalyst complex without prior heating. With prior heating up to reaction temperature, the catalyst leaching is rising enormously. At reaction temperature, the catalyst complex is strongly coordinating to the double bonds of the oleochemicals. Even after cooling the solution down this bonding does not get detached (Fig. 9.4).

The amount of catalyst leaching depends on the type and number of double bonds: conjugated double bond, unconjugated double bond, single double bond, no double bond. The functional group of the molecule does not effect the leaching, so that the results of methyl stearate and n-hexane do not differ.

9.2.4 Application of Ligands

To minimise the strong coordination of the catalyst complex to the fatty compounds the application of ligands is possible. However, it was shown that a minimised catalyst leaching is always combined with a decrease in yield. The only ligand

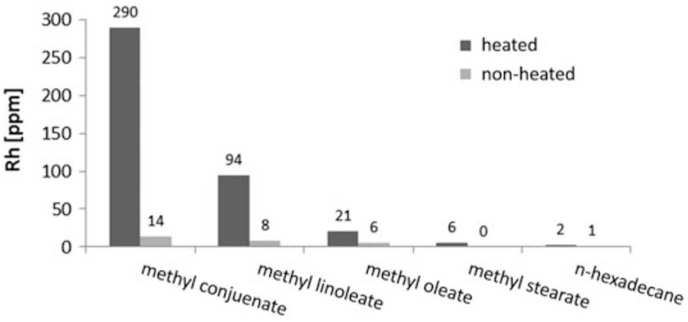


Fig. 9.4 Examination of the solubility behaviour of the catalyst with different unpolar components in two-phase mixtures with and without prior heating [22]. Conditions: *Cat.* $RhCl_3 \cdot 3H_2O$; *Solvent* Propylene carbonate; $w_{unpol.comp.} = 0.5$; $c_{cat.} = 0.5$ mol%; $t = 5$ h; $T = 70$ °C; $T_{Separation} = -5$ °C, RT with methyl stearate)

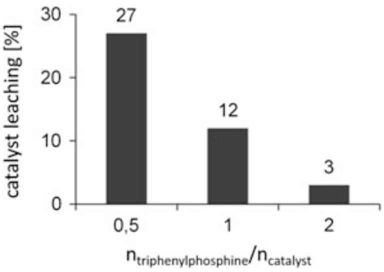


Fig. 9.5 Influence of the triphenylphosphine to catalyst ratio to the catalyst leaching into the product phase. conditions: *Cat.* $RhCl_3 \cdot 3H_2O$; *Ligand* Triphenylphosphine; *Reg.* Crotyl chloride; *Solvent* 1,4-Dioxane and Propylene Cabonate; *Educt* Emery Edenor SB05 (w-% of linoleic acid in educt $w_{\text{linoleic acid}} = 0.62$); $w_{\text{Emery,SB05}} = 0.4$; $w_{\text{Propylene Carbonate}} = 0.4$; $w_{1,4\text{-Dioxane}} = 0.2$; $c_{\text{cat}\cdot} = 1$ mol%; $n_{\text{Reg}}/n_{\text{Kat}\cdot} = 25$; $T_R = 70$ °C; $p_{\text{Ethylene}} = 10$ bar contin.; 750 rpm

which minimises the catalyst leaching in an acceptable manner and still allows moderate conjugation and cooligomerisation is triphenylphosphine [23, 24].

The concentration of the ligand influences the achievable leaching and yield. In general the more ligand is used the lower the leaching and the yield is (Figs. 9.1 and 9.5). An increasing concentration of the ligand leads to a suppressed coordination of the ligand to the fatty compounds. But this effect is simultaneously combined with a suppressed tandem reaction which leads to a loss in yield (Fig. 9.5).

Figure 9.6 shows the yield time curve with different triphenylphosphine (TPP) concentrations. Higher concentrations lead to a suppressed tandem reaction so that a compromise between minimised leaching and moderate yield has to be found. Initially, the recycle of the catalyst has to be proven in continuous operation so it is reasonable to use a ligand concentration of 2 mol%.

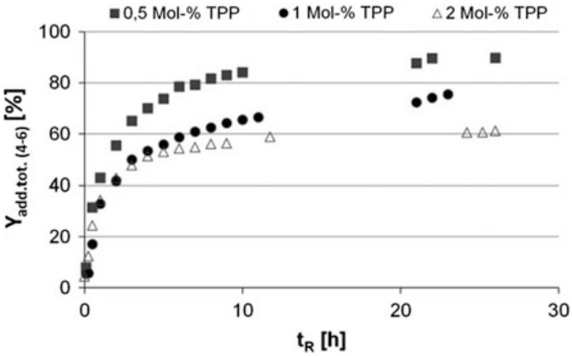


Fig. 9.6 Triphenylphosphine influence to the tandem reaction of cooligomerisation and conjugation of linoleic acid with ethylene [20, 21]. conditions: *Cat.* $RhCl_3 \cdot 3H_2O$; *Ligand* Triphenylphosphine TPP; *Reg.* Crotyl chloride; *Solvent* 1,4-Dioxane and Propylene Cabonate; *Educt* Emery Edenor SB05 (w-% of linoleic acid in educt $w_{\text{linoleic acid}} = 0.62$); $w_{\text{Emery,SB05}} = 0.4$; $w_{\text{Propylene Carbonate}} = 0.4$; $w_{1,4\text{-Dioxane}} = 0.2$; $c_{\text{cat}\cdot} = 1$ Mol-%; $n_{\text{Reg}}/n_{\text{Kat}\cdot} = 25$; $T_R = 70$ °C; $p_{\text{Ethylene}} = 10$ bar contin.; 750 rpm

9.3 Miniplant Investigations

9.3.1 Miniplant Concept for Continuous Operation

Based on laboratory investigations, Witte [21] designed a miniplant concept, which is shown in Fig. 9.7 (block flow chart) and in Fig. 9.8 (process flow chart).

The fatty compounds are dosed together with the solvent dioxane and propylene carbonate from the storage vessel B-01 to the continuous stirred tank reactor (CSTR) B-02 using a piston diaphragm pump P-01 (Fig. 9.9). The loss of solvent according to the ternary diagram in Fig. 9.3 is compensated by continuous dosing so that a constant composition is guaranteed. The continuous pressure of 10 bar is provided by using a pressure reducer. In the separator B-03, the separation of the two phases takes place at 10 °C and 10 bar. CSTR and separator are operated at the same pressure so that the recycle of the catalyst containing polar phase and the recycle of the gas phase can be easily realised.

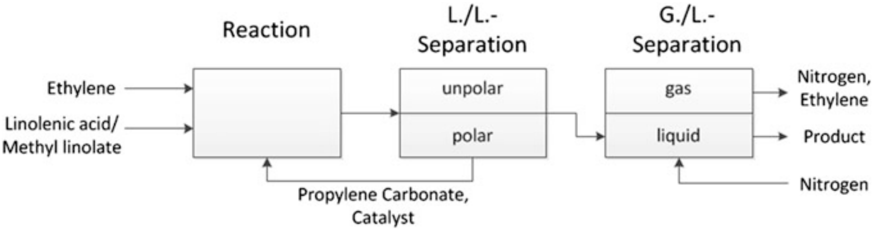


Fig. 9.7 Block flow chart of the designed miniplant for continuous production of branched fatty derivatives

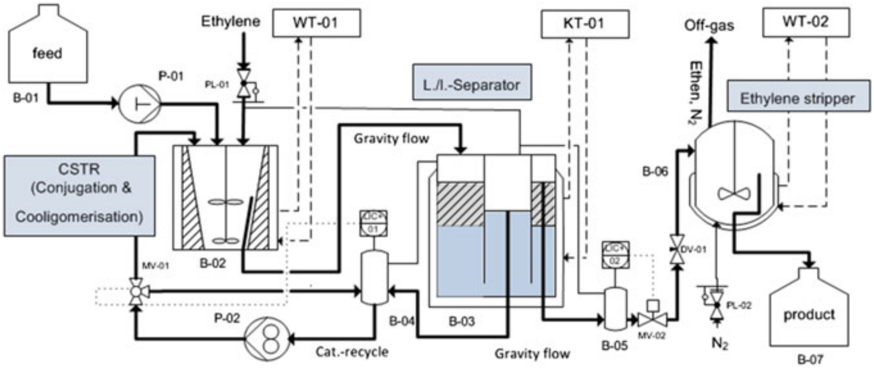


Fig. 9.8 Process flow chart of the designed miniplant for continuous production of branched fatty derivatives [22]

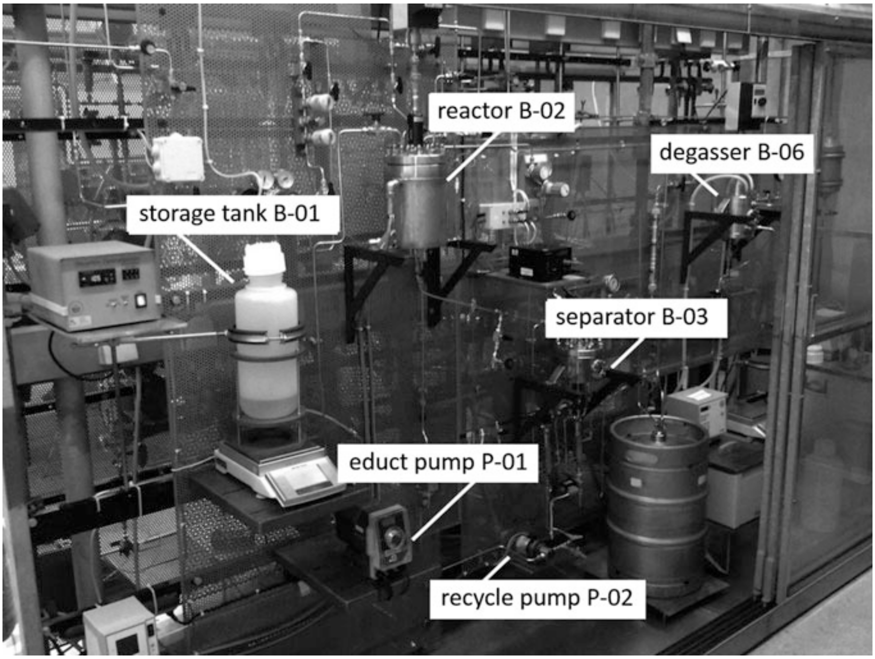


Fig. 9.9 Miniplant for the continuous production of branched fatty

By means of a gear pump P-02, the polar catalyst phase is recycled from the separator back to the CSTR. The unpolar product phase flows pressure controlled from the separator to the stripper B-06 and is expanded to atmospheric pressure. In the stripper, a continuous nitrogen stream removes remaining ethylene at 60 °C. Gravity driven the product phase flows to the product vessel B-07.

The designed, built, and tested miniplant for the continuous production of branched fatty derivatives at the chair of Technical Chemistry is shown in Fig. 9.9.

9.3.2 Miniplant Equipment

9.3.2.1 Vessels

The CSTR B-02 was designed and is based on the shape of a truncated cone with a Volume of approximately 820 ml.

Due to the geometry of the CSTR (Fig. 9.10) high retention times combined with low flow rates are possible. The truncated cone geometry allows small filling volume but still high filling level so that the required mixing of the liquid phase is provided. It is possible to use one or more angled turbine blades depending on the filling level. The respective stirrer blades of the different stirrers are designed for the referring reactor diameters at different filling levels.

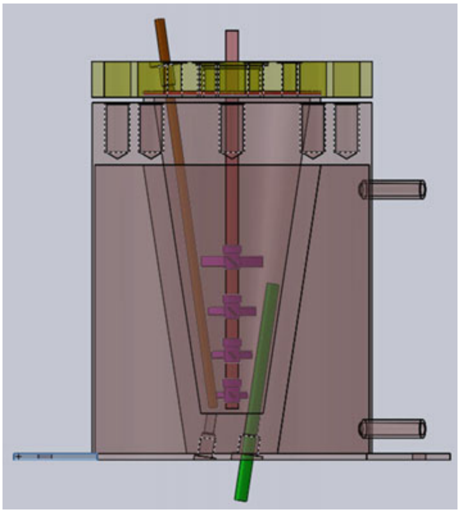


Fig. 9.10 Cross section of the designed CSTR with truncated cone geometry [21]

Separator B-03 and stripper B-06 both are built with cylindrical geometry and can be heated by a double shell like the CSTR. The operating principle of the separator was invented like it is shown in Fig. 9.11. The integrated inner tube in separator B-03 is attached to the vessel lid. The liquid stream from the CSTR flows into the outer area in the separator. The heavy phase gets into the inner tube through a gap at the bottom of the vessel. Due to the density differences the specific heights h1, h2, h3 are adjusted. Through the corresponding risers the phases leave the separator gravity controlled.

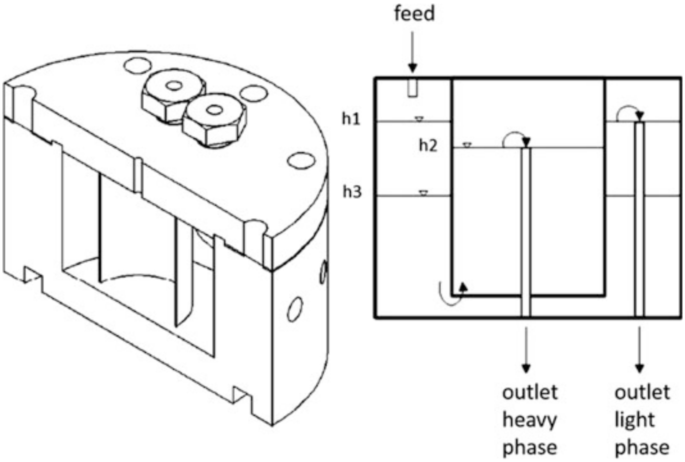


Fig. 9.11 Operating principle of the used separator B-03: The separation of the two phases is realised by the density differences

The acquisition and control of the pumps and thermostats is realised by using the software National Instruments LabView® combined with the hardware interface National Instruments CompactRIO®. The control of the solenoid valves MV-01 and MV-02 (see Fig. 9.8) for the catalyst recycle and the expansion of the product phase is deliberately decoupled from the LabView control system. Those valves are controlled autonomously by an electronic transistor circuit so that it is possible to operate the whole miniplant in continuous manner without using the control system.

9.3.3 Miniplant Operation in Continuous Manner

The optimised reaction conditions from laboratory investigations under continuous pressure can be transferred to the miniplant. To start up, the reactor is run for five hours in batch operation while in continuous operation the retention time is set to 2 h.

The yield time curve is shown in Fig. 9.12 for a continuous 100 h operation. The switch from batch to continuous operation was realised after five hours while a decrease in yield of about 10% is the response. Afterwards the reaction is levelling off in between 22 and 25%.

The stationary plateau indicates that the catalyst was effectively recycled while continuous operation. The catalyst leaching of 2% matches the investigations in laboratory scale.

The recyclability was proven in continuous operation in miniplant, but with the achieved yield of maximum 25% and a catalyst leaching of 2% the process is not

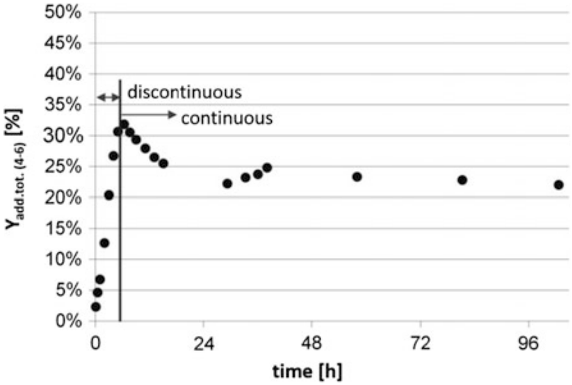


Fig. 9.12 Yield time curve of a miniplant operation for the production of branched fatty derivatives (reactor retention time 20 h). Conditions: *Cat.* $RhCl_3{\cdot}3H_2O$; *Ligand* Triphenylphosphine; *Reg.* Crotyl chloride; *Solvent* 1,4-Dioxane and propylene carbonate; *Educt* Emery Edenor SB05 (w-% of linoleic acid in educt $w_{\text{linoleic acid}} = 0.62$); $w_{\text{Emery,SB05}} = 0.4$; $w_{\text{Propylene Carbonate}} = 0.4$; $w_{1,4\text{-Dioxane}} = 0.2$; $c_{\text{cat.}} = 1$ mol%; $c_{\text{TPP.}} = 2$ mol%; $n_{\text{Reg}}/n_{\text{Kat.}} = 25$; $T_R = 70$ °C; $p_{\text{Ethylene}} = 10$ bar contin.; 750 rpm

economically reasonable. Higher yields can only be achieved by using no ligands which on the other hand leads to a higher catalyst leaching.

Therefore, a process with alternative catalyst recycling was investigated. Like it is shown in Fig. 9.4 the homogeneous catalyst coordinates to the unsaturated compounds. So it is presumed that the coordination will be detached after hydrogenation of the unsaturated, branched, fatty derivatives. Investigations have shown that the rhodium catalyst can be gained back from the saturated, branched, fatty derivatives (Iodine Value = 10) using propylene carbonate as extraction agent. Under optimised conditions, the rhodium leaching can be minimised from 450 ppm (after cooligomerisation without using ligands) to 4 ppm ($m_{\mathrm{PC}}/m_{\mathrm{product\ mixture\ from\ cooligomerisation}} = 1/10$, $T_{\mathrm{Extr.}} = 25$ °C, 4-stage sequential extraction).

9.3.4 Hydrogenation

For the hydrogenation of the branched fatty derivatives, a heterogeneous palladium on activated carbon (1%) catalyst has been found to be most active. The most reasonable solvent concerning achieved iodine value, price, and boiling point is methanol. For the optimisation of pressure and temperature, the rhodium adsorption to the heterogeneous catalyst is from great interest.

Figures 9.13 and 9.14 show the Rhodium concentration of the product phase after hydrogenation as a function of pressure and temperature. The lower the pressure and temperature are, the higher the Rhodium content in the product mixture is after hydrogenation. According to the results, the rhodium adsorption is strongly depending on the preset pressure and temperature, so in miniplant scale it is reasonable to operate with low pressure and low temperature. Further experiments show that the pressure has a slight effect on iodine value, while 5 and 10 bar lead to slightly lower iodine values there was no difference found between 20 and 50 bar (Iodine value = 35). The temperature dependence is almost negligible, so that after one hour there is no difference between iodine values for hydrogenation at temperatures between 25 and 90 °C.

9.3.5 Optimised Miniplant Concept

Figure 9.15 illustrate the flow chart of the optimised process for the production of the saturated, branched, fatty derivatives and Fig. 9.16 shows the corresponding process flow chart.

The product mixture from the cooligomerisation process is mixed with methanol in a buffer tank (B-07) and then dosed to the trickle bed reactor consisting of tree sequential tubular reactors (B-08). The saturated mixture is then expanded to atmospheric pressure and in the stripper B-09 a continuous nitrogen stream removes remaining hydrogen. The next step is the distillation (B-11) to separate and recycle

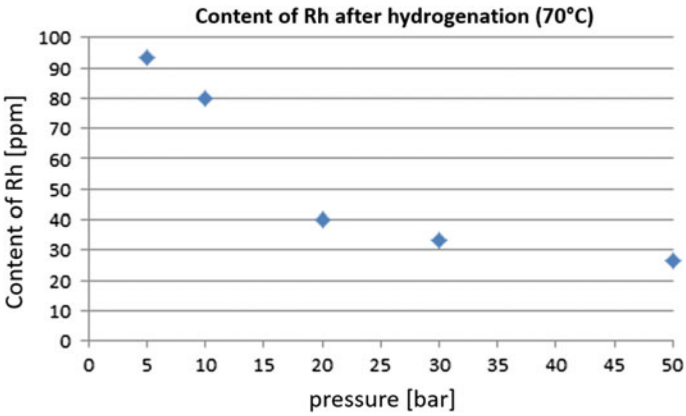


Fig. 9.13 Rhodium content in the product mixture after hydrogenation in function of the pressure. Conditions: *Hydrogenation* Pd/C 1%; *Solvent* Methanol; T_R = 70 °C; 100 rpm, m_{Cat} = 1 g, conti pressure *Conditions* cooligomerisation.: *Cat.* $RhCl_3$ $3H_2O$; *Reg.* Crotyl chloride; *Solvent* 1,4-Dioxane and Propylene Cabonate; *Educt* methyl linoleate (w-% of methyl linoleate in educt $w_{\mathrm{methyl\ linoleate}} = 0.59$); $w_{\mathrm{methyl\ linoleate}} = 0.4$; $w_{\mathrm{Propylene\ Carbonate}} = 0.4$; $w_{1,4\text{-}\mathrm{Dioxane}} = 0.2$ $c_{\mathrm{cat.}} = 1$ mol%; $n_{\mathrm{Reg}}/n_{\mathrm{Cat.}} = 25$; T_R = 70 °C; p_{Ethylene} = 10 bar contin; 750 rpm, $T_{\mathrm{Separation}}$ = 10 °C, L_{Rh} = 450 ppm

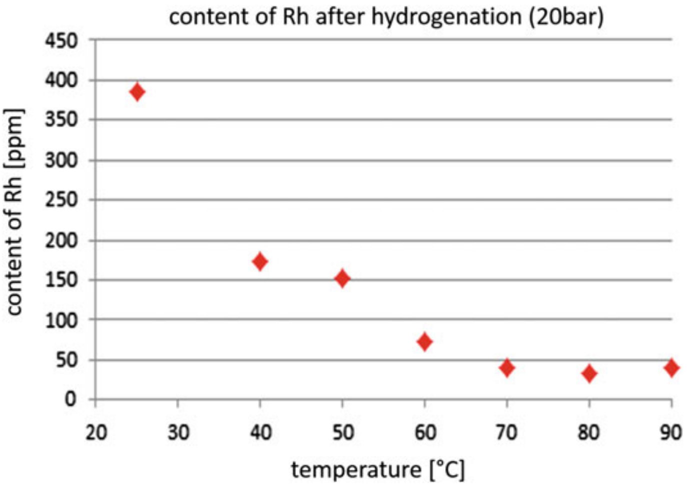


Fig. 9.14 Rhodium content in the product mixture after hydrogenation in function of the temperature [22]. Conditions: *Hydrogenation* Pd/C 1%; *Solvent* Methanol; p_{H2} = 20 bar conti; 100 rpm, m_{Cat} = 1 g, *Conditions* cooligomerisation.: *Cat.* $RhCl_3$ $3H_2O$; *Reg.* Crotyl chloride; *Solvent* 1,4-Dioxane and Propylene Cabonate; *Educt* methyl linoleate (w-% of methyl linoleate in educt $w_{\mathrm{methyl\ linoleate}} = 0.59$); $w_{\mathrm{methyl\ linoleate}} = 0.4$; $w_{\mathrm{Propylene\ Carbonate}} = 0.4$; $w_{1,4\text{-}\mathrm{Dioxane}} = 0.2$ $c_{\mathrm{cat.}} = 1$ mol%; $n_{\mathrm{Reg}}/n_{\mathrm{Cat.}} = 25$; T_R = 70 °C; p_{Ethylene} = 10 bar contin; 750 rpm, $T_{\mathrm{Separation}}$ = 10 °C, L_{Rh} = 450 ppm

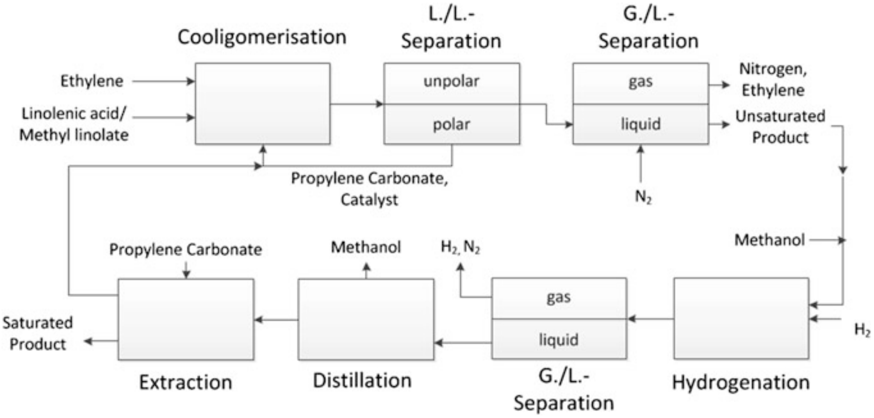


Fig. 9.15 Flow Chart of the optimised process for the production of saturated, branched, fatty derivatives

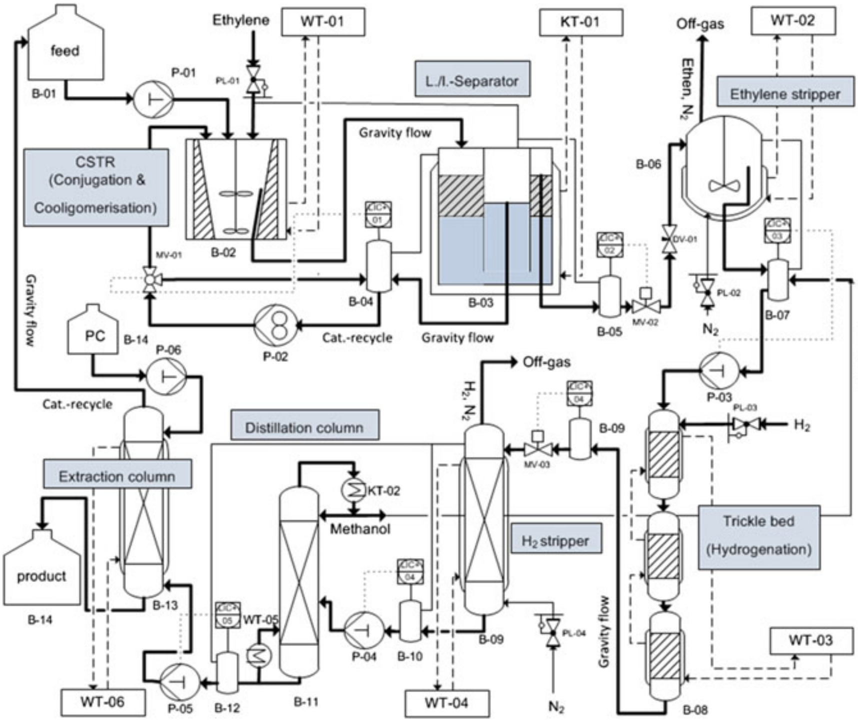


Fig. 9.16 Process flow chart of the designed miniplant for the optimised continuous production of branched fatty derivatives

the methanol used for the hydrogenation step. After separating the mixture from methanol the last unit is the extraction of the remaining homogeneous rhodium catalyst using propylene carbonate as extracting agent. The extracted catalyst recycle can then be dosed to the feed storage. The additional propylene carbonate is supposed to compensate the solvent loss in the liquid–liquid separator (B-03).

The hydrogenation step was studied in detail. While palladium catalyst is able to hydrogenate the branched unsaturated products **4-6**, the leached rhodium from the homogeneous catalysed cooligomerisation is precipitated on the surface of the heterogeneous catalyst. This indicates that the product quality is not suffering from rhodium loadings any further. The trickle bed was operated for 100 h and showed a stable behaviour. A rhodium doped catalyst was found after this experiment.

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Chapter 10
Hydroamination and Telomerisation of *β*-Myrcene

T. Färber, Arno Behr and Andreas J. Vorholt

10.1 Introduction

In this chapter, the scale-up of the hydroamination (see Chap. 4) and telomerisation (see Chap. 5) of the industrially available renewable resource *β*-myrcene (hereafter simply called myrcene) from batch to a continuous process is discussed in detail. The terpenyl amines produced by these reactions could be used as plasticisers, as precursors for surfactants or even as fragrances, depending on the substrate combination. This enables an alternative route to these interesting products. The variety of products that can be generated from the renewable starting material myrcene is depicted by Behr and Hu [1, 2].

The hydroamination is an atom-economical reaction for the synthesis of alkyl amines via formation of a C–N bond. The hydroamination can be carried out intramolecularly, resulting in heterocycles or intermolecularly, when amine and unsaturated compound are separate molecules (Fig. 10.1). This offers an alternative route to alkyl amines apart from the common paths such as oxidation of the unsaturated compound and condensation with an amine [2].

While the reaction of an alkene with an amine is thermodynamically feasible, it suffers from a very high activation barrier. This is caused by the repelling effect of the π-electron cloud of the alkene with the free electron pair of the amine [4]. However, without a catalyst the application of higher temperatures to overcome this activation barrier results in a shift in the chemical equilibrium towards the starting materials, thus limiting the total conversion of the reaction. At this point, a highly active catalyst is needed to lower the activation barrier and to facilitate the hydroamination at lower temperatures.

The hydroamination can be catalysed by a wide variety of catalysts, including acid/base-catalysts, metal and late transition metal catalysts as well as alkali and rare earth metals. A good overview about the scope of hydroamination catalysts and substrates is given by Müller et al. [5]. The *Takasago* process, one of the rare realisations of the hydroamination on industrial scale (5000 t/a (-)-menthol),

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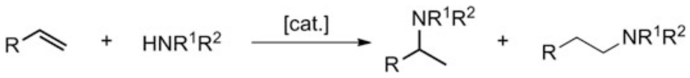

Fig. 10.1 Hydroamination of an alkene with an amine [3]

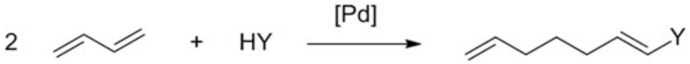

Fig. 10.2 Telomerisation reaction of a diene (exemplified by butadiene)

incorporates the lithium-catalysed hydroamination of myrcene with diethylamine to *N,N*-diethylgeranylamine [6]. Late transition metals like palladium or platinum combined with phosphorus or carbene ligands feature greatly improved catalytic activity [5], but require an efficient catalyst recycling as a result of higher catalyst prices. The hydroamination of myrcene with morpholine to the desired terpenyl amines is shown in detail in Fig. 10.3 (see Chap. 4).

In contrast to the hydroamination, the telomerisation incorporates two diene molecules and one molecule of the nucleophilic component. The telomerisation is defined as a diene oligomerisation with the incorporation of a nucleophile. Like the hydroamination, it is an atom-economic coupling reaction leading to the desired terpenyl amines, but with two molecules of the diene incorporated into the final product (Fig. 10.2).

Like the hydroamination, the telomerisation can be catalysed by transition metals, for example, palladium, platinum, or nickel [7]. An overview of the wide catalyst and substrate spectrum used in the telomerisation is given by Behr et al. [7, 8]. The telomerisation reaction and the scope of possible substrates and nucleophiles are

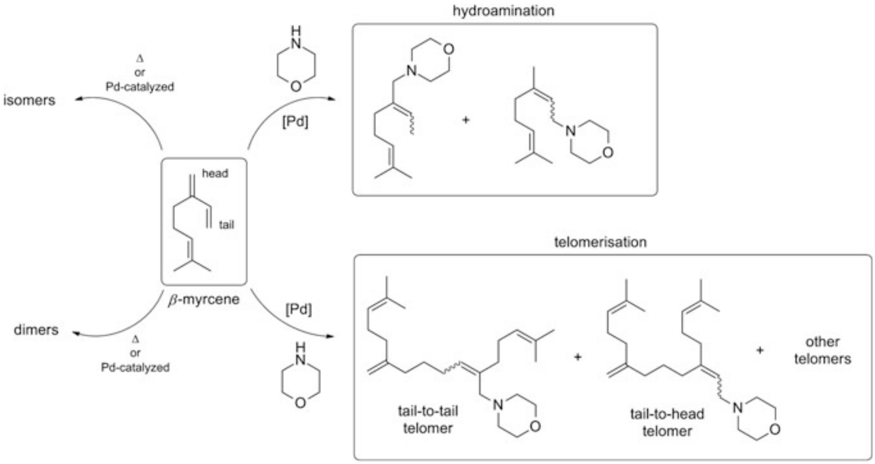

Fig. 10.3 Product spectrum of the hydroamination and telomerisation of *β*-myrcene

described in detail in Chap. 5. Figure 10.3 shows the hydroamination and telomerisation of myrcene with morpholine as well as the isomerisation and dimerisation side-reactions.

It has to be noted that both reactions can be catalysed by the same or similar catalytic system and incorporate the same substrates, so the path of the reaction has to be controlled by the reaction parameters.

10.2 Laboratory Experiments

10.2.1 Control of Reaction Pathways

The desired pathways of hydroamination and telomerisation as well as the side-reactions isomerisation and dimerisation are illustrated in Fig. 10.3. It has to be noted that both side-reactions can either be favoured by heat or the palladium complex. Compared to the main reactions, these reaction pathways can in most cases be suppressed by not exceeding a certain temperature level.

The hydroamination and telomerisation can be catalysed by the same catalytic system, so the control of the reaction pathways is of great concern. Johnen conducted an extended catalyst screening for the hydroamination of myrcene with morpholine as well as the telomerisation of myrcene with diethylamine. All experiments have been carried out using toluene as the solvent. The best catalytic activity for the hydroamination is achieved by fluorinated palladium precursors as ($Pd(tfa)_2$ or $Pd(hfacac)_2$) in combination with diphosphine ligands (DPPB, DPEPhos) [9]. The telomerisation of myrcene can be catalysed by the same precursor/ligand systems as the hydroamination, but also non-fluorinated precursors ($[Pd(MeCN)_4](BF_4)_2$) and monodentate ligands like triphenylphosphine (TPP) have proven to be active [10].

Apart from the catalytic system, the product spectrum can be influenced by the temperature as well. Johnen varied the reaction temperature for the hydroamination of β-myrcene using $Pd(tfa)_2$/dppb as the catalytic system and points out that good yields of hydroamination products (1,4-adducts) can be achieved at 100–120 °C. However, the dimerisation and isomerisation side-reactions occur in substantial amounts, when a reaction temperature of at least 120 °C is applied (Fig. 10.4, [9]). This concurs with a partial deactivation of the catalyst resulting in the formation of palladium black as a precipitate. This limits the maximum reaction temperature of this catalyst system to 110 °C.

In general, the hydroamination is favoured by high catalyst and ligand concentrations as well as high amine/myrcene ratios. This effect is due to the probability of two myrcene molecules coordinating simultaneously at the active catalytic complex, so that before mentioned conditions shift the reaction system towards the hydroamination products (Table 10.1).

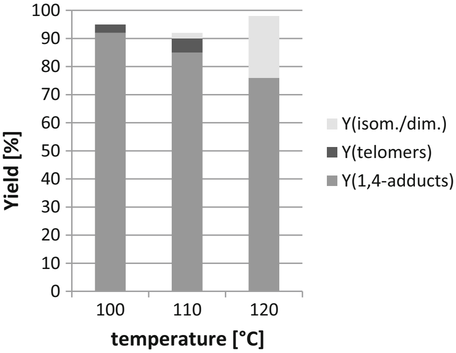

Fig. 10.4 Influence of temperature on the hydroamination of β-myrcene using Pd(CF_3CO_2)$_2$/dppb [9]. Conditions: 0.2 mol%, Pd(CF_3CO_2)$_2$, DPPB, Pd/P 1:8, $t = 5$ h, 500 rpm, c(substrates) = 0.17 mol/l, toluene, p(argon) = 5 bar

Table 10.1 Influencing parameters/reaction conditions on reaction pathway

Parameter	Hydroamination [9]	Telomerisation [10]
Catalyst concentration	0.4 mol% (high)	0.05 mol% (low)
Phosphor:metal ratio	8:1 (high)	$\leq$4:1 (low)
Amine:myrcene ratio	$\geq$1:1	$\leq$1:2
Catalyst	Fluorinated palladium precursors (Pd(tfa)$_2$, Pd(hfacac)$_2$)	Palladium precursors ([Pd(MeCN)$_4$](BF$_4$)$_2$, Pd(tfa)$_2$)
Ligands	Bidentate (DPPB, DPEPhos)	Bidentate or monodentate (DPPB, TPP, Carbene)

The most significant factor to shift the reaction between hydroamination and telomerisation is the catalyst to substrate ratio. An increase in the catalyst concentration leads directly to an increase in hydroamination products (Fig. 10.5).

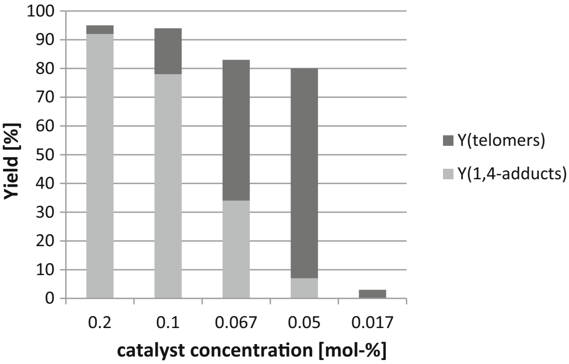

Fig. 10.5 Influence of catalyst concentration on hydroamination and telomerisation product distribution [9]. Conditions: Pd(CF_3CO_2)$_2$, DPPB, Pd/P 1:8, $T = 100$ °C, $t = 5$ h, 500 rpm, c(substrates) = 0.17 mol/l, toluene, p(argon) = 5 bar

10.2.2 Catalyst Recycling

As mentioned in the previous paragraph, the recycling of the homogeneous transition metal catalyst is important for the realisation of the hydroamination and telomerisation on a technical scale. In this case, thermal processes cannot be applied, either because of the product properties (high boiling point, polarity) or catalyst instability at separation temperature. A lot of promising alternative concepts have been developed in recent years to recycle homogeneous catalysts [3]. Especially, thermomorphic solvent systems offer a number of advantages in comparison with multiphase systems. TMS-systems utilise the temperature-dependant miscibility gap between solvents of different polarity. This way the reaction can be performed at elevated temperatures in homogeneous conditions, while the catalyst separation occurs at biphasic conditions at lower temperatures.

The two main aspects for the successful development of a TMS-system are catalysis and phase properties. Johnen investigated two TMS recycling systems for the hydroamination (acetonitrile/*n*-heptane, dimethylformamide/*n*-heptane) and one system for the telomerisation of myrcene (methanol/*n*-octane) in detail. The solvent scope for the polar solvent was then further extended for the hydroamination. For all experiments, *n*-heptane was used as the non-polar phase, while the polar solvent was modified. A wide range of solvents was tested and those solvents, which successfully formed a TMS-system in a suitable temperature range, were applied and tested in the hydroamination reaction. Figure 10.6 shows the influence of the polar solvent on the catalytic activity for the selected solvents.

This exemplifies the impact the choice of solvent can have on the performance of a catalytic system. Acetonitrile, methanol, and *N*,*N*-dimethylformamide (DMF) are active in the hydroamination with decreasing conversion; however, some telomerisation products are formed when using DMF as polar solvent. When methanol is used as the catalyst solvent, the precipitation of palladium black can be observed

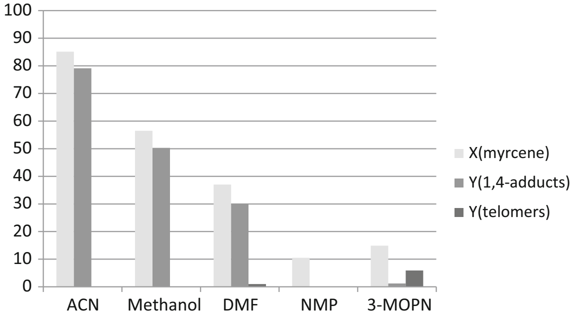

Fig. 10.6 Effect of polar solvent on hydroamination and telomerisation. Conditions: $Pd(CF_3CO_2)_2$/DPPB, $c_{cat.} = 0.4$ mol%, *M/P* = 1:8, $p_{Ar} = 5$ bar, *T* = 110 °C, c(substrates) = 0.1667 mol/l, 450 rpm, *t* = 3 h; *ACN* acetonitrile, *DMF* dimethylformamide, *NMP* *N*-Methyl-2-pyrrolidone, 3-*MOPN* 3-Methoxypropionitrile

after the reaction. As a result, methanol was excluded for the continuous experiments and acetonitrile and DMF were selected for the continuous miniplant experiments.

10.3 Miniplant Investigations

10.3.1 Choice of Reactor

After the catalytic system has been screened in the laboratory, the reaction was transferred into a continuous process in order to look at catalyst recycling and scale-up effects. A very important decision is the correct choice of the chemical reactor. Continuously operated chemical reactors can in most cases be traced or seen as a combination of the two ideal reactor types: continuous stirred-tank reactor (CSTR) and plug-flow reactor (PFR). Each of these reactor types has its specific benefits and disadvantages.

A CSTR would not be suited for a reaction system with consecutive reactions, as the constant presence of all reactants would lead to considerable by-product formation. The hydroamination and telomerisation do not require excessive mixing (homogeneous solution) or gas supply (no gaseous reactants), so a continuous CSTR would not be beneficial, as this would also reduce the overall yield as a result of the continuous dilution by the reaction feed. A CSTR-cascade would compensate this drawback, but also increase the investment costs (multiple reactors, process control equipment) and the costs of operation.

The reactor for the realisation of hydroamination and telomerisation would possess plug-flow behaviour to achieve high yields of the desired terpenyl amines. However, preliminary studies in miniplant-scale have shown that a PFR was not the best option as a result of the low volumetric flow ($\sim$120 ml/h). This low flow rate leads to a very small velocity in the PFR resulting in extreme boundary effects. These effects lead to a very broad residence time distribution and would require a very long reactor (40 m) to reach the desired product yield, resulting in high instrument costs and challenging process operation (heating, cleaning). Higher flow rates on the other hand would increase the costs of the miniplant operation.

A very promising reactor concept to solve this conflict is the so-called Taylor-Couette reactor (TCR). This reactor type combines the advantages of PF and CST reactors and achieves plug-flow like behaviour even at low flow rates.

10.3.2 The Taylor-Couette Reactor

Apart from the “standard”-reactor types, a variety of reactors exists that feature characteristics in between these ideal reactor types (e.g. cascade, loop reactor).

A very promising and versatile reactor is the so-called Taylor-Couette reactor (TCR). It combines the specific advantages of a CSTR (mixing properties) and PFR (plug flow profile). The TCR exhibits a hydrodynamic behaviour closely related to a CSTR-cascade with a very high number of reactors in series, but with the possibility to change the hydrodynamic properties independent of the flow rate. This way the reactor can be tailored to the demands of a specific reaction without changing the reactor hardware (Fig. 10.7).

The TCR consists of two concentric cylinders, which rotate in relation to each other. In most cases the outer cylinder remains static, while the inner one rotates at a certain velocity. This movement results in a number of flow regimes in the annular gap. This creates an additional degree of freedom in comparison with a plug-flow reactor, because the flow conditions can be modified independently of the feed rate.

Apart from a cylindrical rotor, other geometries have been discussed in the literature. Kraushaar-Czarnetzki et al. developed a ribbed rotor that exhibits an even narrower residence time distribution than the standard rotor by "locking" the vortices in place, only allowing for very small mass transfer between the individual reaction volumes [11]. Sorg et al. modified the TCR with a lobed rotor geometry for application as a bioreactor, minimising the hydrodynamic stress in the reaction medium [12].

The advantages of low back-mixing, good heat dissipation, and low shear stress while still remaining good mixing, lead to a variety of possible applications for this reactor type. Among others, its use in polymerisation [13], electrochemical [14], photochemical [15], and enzymatic [11] reactions as well as gas–liquid reactions [16] has already been investigated. The possibility to create a PFR-like flow profile

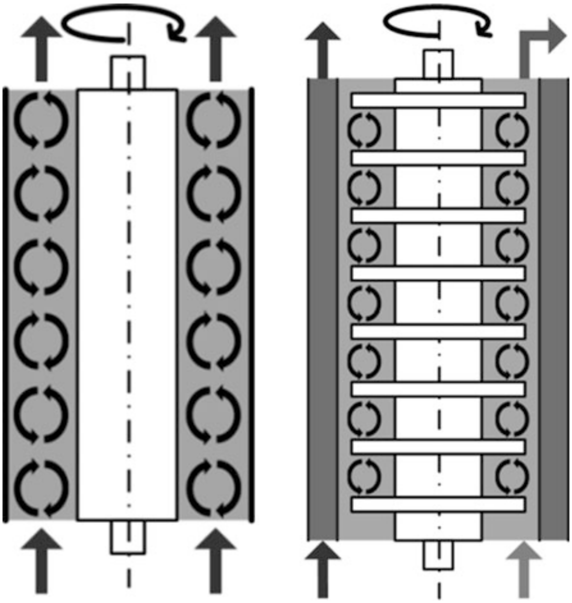

Fig. 10.7 Taylor-Couette reactor with cylindrical rotor (*left*) and ribbed rotor (*right*)

in a well-mixed reactor with good heat transfer makes this reactor a promising concept for the application in homogeneous catalysis as well.

10.3.3 Design Aspects and Construction

The main focus of this work is the transfer of a homogeneous process from laboratory batch experiments to a continuously operated process. As a result, the optimisation of the TCR was not the main goal; instead the main focus lied upon the application of this reactor concept in the field of homogeneous catalysis. Basis of the reactor development were the works of Richter and Liu, which conducted extensive research in the field of Taylor-Couette reactor development and its use for polymer synthesis [11, 13, 17]. Based on these works we scaled-up and developed a TCR with a ribbed rotor, which was specifically tailored towards our demands in homogeneous catalysis. The final technical drawing of the TCR is shown in Fig. 10.8. The reactor features a pipe-in-pipe heating system with an external thermostat. It can be operated up to a pressure of 5 bar, which is needed for the inert atmosphere and to keep the organic solvents in the liquid phase at reaction temperature. The bearing of the rotor is achieved by a fixed/floating bearing system in the upper part of the reactor, sealed by two graphite-filled Teflon-seals. The rotor is connected to a magnetic coupling on top of the reactor which is driven by an electric motor.

After construction of the TCR residence time measurements were made to verify the flow characteristics of the reactor. Experiments with varying flow rate and

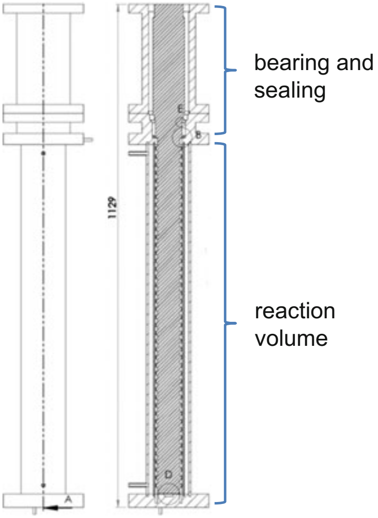

Fig. 10.8 Technical drawing of the constructed Taylor-Couette reactor

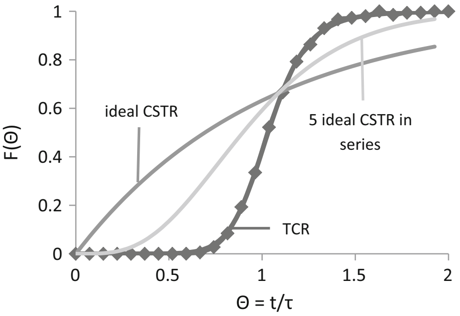

Fig. 10.9 Taylor-Couette reactor flow characteristics

rotational speed showed that the flow characteristics were similar to a CSTR-cascade with a high number of reactors in series (Fig. 10.9).

10.3.4 Batch Experiments

After the flow characteristics of the TCR were examined, the performance in homogeneously catalysed reactions had to be investigated. The reactor was mounted and connected to two high precision HPLC pumps for dosing of the liquid components. The hydroamination was carried out in a homogeneous solution with toluene as solvent (no TMS-system), as it showed the best results in the laboratory screening experiments [9]. The catalytic system ($Pd(tfa)_2$/DPPB) was used as a benchmark system. This system was developed by *Johnen* and already showed high catalytic activity in the hydroamination of myrcene. Figure 10.10 shows a comparison of the hydroamination in a laboratory batch reactor (*Parr* pressure autoclave) and the Taylor-Couette reactor under similar reaction conditions.

The Taylor-Couette reactor is able to reproduce the batch experiments with comparable hydroamination yields (X(myrcene) = 97%, Y(1,4-adducts) = 87%). The slight increase in side-product formation is most likely a result of the non-ideal temperature distribution along the length of the reactor. As a result, the TCR tempering jacket was retrofitted with guide plates to achieve a more even temperature distribution.

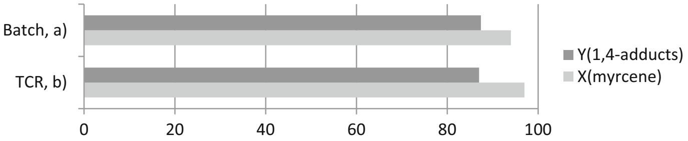

Fig. 10.10 Results of the hydroamination in batch- and Taylor-Couette reactor. Conditions: *solvent* toluene, $Pd(CF_3CO_2)_2$/DPPB, c(cat.) = 0.454 mol%, M/P = 1:8, p(argon) = 5 bar, T = 110 °C, c(substrates) = 0.1667 mol/l, (**a**) TCR: 100 rpm, τ = 4 h; (**b**) batch: 450 rpm, t = 3 h, V(solvent) = 100 ml

10.3.5 Miniplant Concept

After the catalytic activity of the TCR in the hydroamination has been tested, the reactor was integrated into the miniplant and connected to the peripherals. A simplified version of the process flow chart is shown in Fig. 10.11 and illustrates the necessary process equipment for the continuous operation of the reactor and the continuous recycling of the catalyst using TMS-systems. The miniplant is equipped with a process monitoring system (*National Instruments* CompactRIO) to monitor the necessary process parameters (p, T, m) with *NI* LabVIEW.

Fluid transport is achieved by HPLC pumps for the precise dosing of the substrates and a diaphragm pump for the non-polar solvent. The catalyst phase is placed in the phase separator at the beginning of the reaction and dosed by a HPLC pump. All the liquid components (solvent, substrates, and catalyst phase) are fed into a heated mixing unit that homogenises the mixture, but operates below reaction temperature. This way a precise ratio of catalyst to substrates can be set, as *Johnen* already showed that the catalyst to myrcene ratio is one of the key factors to shift the reaction system between hydroamination and telomerisation [18]. The homogenous solution is fed into the Taylor-Couette reactor and the reaction proceeds (T_{reaction} = 100–110 °C). After the specified residence time, the mixture leaves the reactor at the top and flows gravity-driven into the cooled phase separator (T = 10 °C), where the mixture splits into the polar catalyst phase, which is fed back into the reactor and the non-polar product-rich phase which is continuously

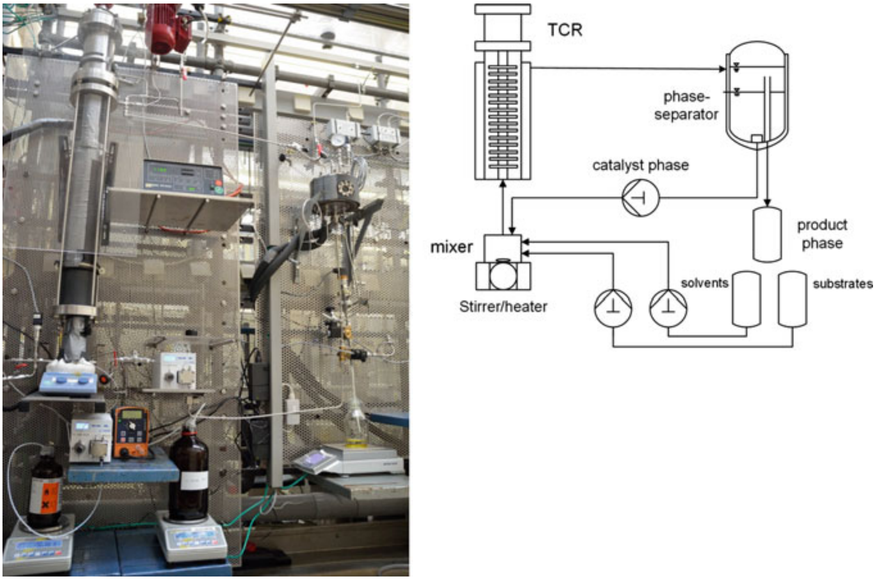

Fig. 10.11 Integration of Taylor-Couette reactor and miniplant peripherals

discharged by an autonomous system and weighed. The product phase can then be analysed by GC-chromatography.

10.3.6 Continuous Experiments

Two main TMS-systems for hydroamination and telomerisation were first briefly tested by Johnen and later optimised. The TMS-systems acetonitrile (ACN)/*n*-heptane and dimethylformamide (DMF)/*n*-heptane were both active and showed low catalyst leaching (Table 10.2) but differed in the selectivity towards hydroamination and telomerisation. These two systems were then tested in continuous experiments in the miniplant. The results are shown in Figs. 10.12 and 10.13.

Table 10.2 Average catalyst leaching into the non-polar product phase during miniplant operation

Element	TMS-system catalyst leaching	
	Acetonitrile/*n*-heptane	Dimethylformamide/*n*-heptane
Pd [ppm]	3(0.6%)	2(0.5%)
P [ppm]	6(0.9%)	4(0.5%)

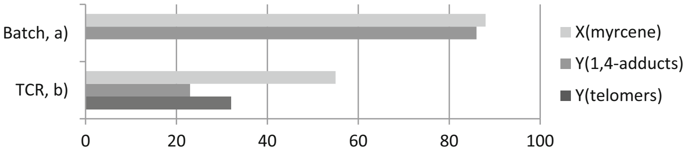

Fig. 10.12 Comparison of batch and miniplant experiments (TMS-System: ACN/*n*-heptane). Conditions: *TMS-System* acetonitrile/*n*-heptane (40:60), $Pd(CF_3CO_2)_2$/DPPB, *c*(cat.) = 0.454 mol%, *M/P* = 1:8, p(argon) = 5 bar, *T* = 110 °C, c(substrates) = 0.1667 mol/l, (**a**) TCR: 100 rpm, *T* = 4 h; (**b**) batch: 450 rpm, *t* = 3 h

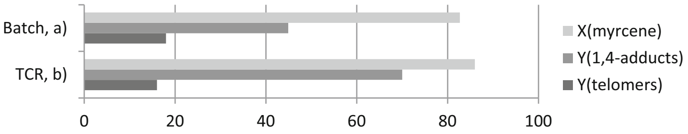

Fig. 10.13 Comparison of batch and miniplant experiments (TMS-System: DMF/n-heptane). Conditions: *TMS-System* dimethylformamide/*n*-heptane (40:60), $Pd(CF_3CO_2)_2$/DPPB, *c*(cat.) = 0.454 mol%, *M/P* = 1:8, p(argon) = 5 bar, *T* = 110 °C, c(substrates) = 0.1667 mol/l, (**a**) TCR: 100 rpm, *T* = 4 h; (**b**) batch: 450 rpm, *t* = 3 h

The results of the ACN/*n*-heptane system differ significantly from the laboratory results. The catalyst activity and selectivity towards the hydroamination products are very low. However, large amounts of telomerisation products are formed, which is a strong indicator, that either the ligand concentration in the catalyst phase or the overall catalyst concentration is too low. This controlling effect was also observed by *Johnen* and in previous laboratory experiments (Fig. 10.5). The reaction system can be shifted between hydroamination and telomerisation by catalyst and ligand concentrations, where low concentrations favour the telomerisation [9, 10]. During miniplant operation, the precipitation of ligand could be observed at the interface between the two solvents in the phase separator. It was conducted that the solubility of the ligand DPPB in the solvent acetonitrile is too low, so precipitation occurs when the catalyst phase is cooled down after the reaction. This behaviour was not observed in the laboratory because of the different preparation procedures and temperatures. As a result the alternative system DMF/*n*-heptane was tested, as the polar solvent DMF possesses significantly better solubility for the catalyst system. The results of the miniplant experiment with the TMS-system DMF/*n*-heptane are shown in Fig. 10.13. Only the polar solvent was changed in comparison with the previous experiment, all other process parameters remained unchanged.

The activity of the system is significantly increased in comparison with the acetonitrile-based TMS-system. With a myrcene conversion of 86 and 70% yield of hydroamination products, the performance of the laboratory experiments can be reproduced and even be exceeded. The formation of small amounts of telomers is a result of the coordinating nature of the polar solvent DMF, which can also act as a ligand in the catalytic system and was also observed in batch experiments (Fig. 10.6). The comparison of both TMS-systems illustrates the importance of the solvent for the performance of the catalyst.

Another important aspect of every continuous process is the loss of the catalyst into the product phase (catalyst leaching). It has a massive impact on the economy of a process and can determine if a process is realised or rejected. Both TMS-systems tested in the continuous hydroamination and telomerisation show low catalyst leaching (Table 10.2) which shows that TMS-systems can be a demanding but effective tool for catalyst recycling. However, the TMS-system has to be tailored to the demands of each chemical reaction (polarity, effects on catalysis) and not all effects can be determined in batch experiments. This shows the importance of continuous experiments in the development of new catalytic processes with renewable resources.

10.4 Conclusion and Outlook

The transfer of a chemical reaction from batch to continuous scale poses a great challenge as a result of the variety of influencing factors that have to be considered. In addition to the catalysis, aspects such as solubility, catalyst recycling and handling have to be taken into consideration. The combination of hydroamination and telomerisation of the renewable *β*-myrcene with TMS-systems allows the atom-efficient synthesis of terpenyl amines and the efficient recycling of the precious transition metal catalyst.

For the production of terpenyl amines, a Taylor-Couette reactor has been implemented into a miniplant with continuous catalyst recycling by thermomorphic multicomponent solvent systems. High yields of the desired products (70% 1, 4-adducts, and 16% telomers) were generated while maintaining a leaching of only 2/4 ppm Pd/P in the TMS-system DMF/*n*-heptane. This shows that the TCR is a promising reactor concept for homogeneous catalysis, as it combines the advantages of CSTR (good mixing) and PFR (plug-flow behaviour with low back-mixing).

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Chapter 11
Continuously Operated Hydroformylation

J. Dreimann, Arno Behr and Andreas J. Vorholt

11.1 Introduction

As described in Chap. 3, hydroformylation is one of the most important applications for homogeneous catalysis. Industrial proven processes like the Ruhrchemie/Rhône-Poulenc-Process (RCh-RP) are based on a fossil feedstock mainly producing the linear *n*-butanal. The use of an aqueous/organic two-phase system leads on the one hand to high selectivities of C_4-aldehydes and on the other hand to a highly efficient recovery of the precious rhodium catalyst complex. This process is not applicable for higher olefins ($>C_5$) due to their low solubility in the aqueous catalyst phase [1].

In order to develop processes for homogeneously catalysed reactions using renewable feedstocks, not only just reaction parameters and catalyst complexes have to be optimised but also innovative catalyst recycling concepts are imminent for economic operation. The hydroformylation of 1-dodecene in a continuously operated miniplant is the first step towards novel industrial processes using renewables. Terminal hydroformylation of olefins with internal C=C double bonds as well as hydroformylation of higher functionalised substrates with a terminal C=C double bond are tackled to combine both approaches in the isomerising hydroformylation of higher functionalised substrates. Figure 11.1 shows the pathway of reactions to reach, e.g. the continuous hydroformylation of methyl oleate.

Several approaches have been made to combine the hydroformylation of long chain olefins with a highly efficient catalyst recycling. Therefore investigations on the phase behaviour using surfactants, supercritical liquids or ionic liquids have been conducted [2]. Another possibility of catalyst retention is using a novel separation concept like organic solvent nanofiltration [3].

The process concept in the following is based on the thermodynamic behaviour of the mixture of one polar and one apolar solvent. The used solvents have a highly temperature-dependent miscibility gap, so that one single liquid phase is present at

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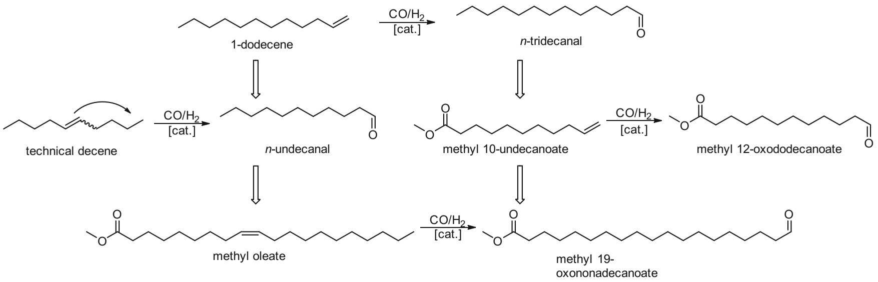

Fig. 11.1 Steps of the process development

higher reaction temperature and two phases, one containing the substrate and products and one containing the catalyst complex, are present at lower temperature.

11.2 Batch Investigations: Catalyst Screening and Catalyst Recycling

The first step in the process development described here is the selection of an appropriate catalyst complex consisting of the catalyst precursor and the ligand. First, the model hydroformylation of 1-dodecene has been carried out in batch experiments (Table 11.1).

From several rhodium precursors (Acetylacetonato)dicarbonylrhodium(I) (Rh(acac)$(CO)_2$) was chosen as reference and was used for further optimisation. High yields of the linear product *n*-tridecanal **2** and high *n/iso*-ratios are favourable. The use of the unmodified rhodium precatalyst Rh(acac)$(CO)_2$ and reference conditions leads to a conversion X of 1-dodecene **1** of 55%, whereas the yield Y of *n*-tridecanal is at 11% and a *n/iso*-ratio of 40/60 is reached. Besides the hydroformylation to branched aldehydes **3**, isomerisation to internal olefins **4** and hydrogenation to dodecane **5** are side reactions, as presented in Fig. 11.2.

In order to optimise the reaction towards higher *n*-tridecanal yields and *n/iso*-ratios, a wide ligand screening is carried out [4–6]. Figure 11.3 shows the

Table 11.1 Reference conditions

$n_{\text{1-dodecene}}$	0.0068 mol/1.14 g
$n_{\text{Rh(acac)(CO)2}}$	$6.8 \cdot 10^{-6}$mol
$n_{\text{1-dodecene}}:n_{\text{Rh}}$	1000:1
V_{toluene}	8.5 mL
F	650 rpm
$p(CO:H_2)$	20 bar (1:1)
T	100 °C
t	2 h

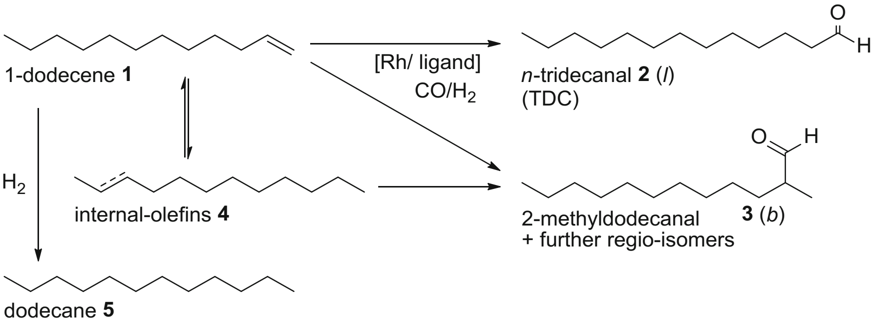

Fig. 11.2 Reaction scheme consisting of hydroformylation, isomerisation, and hydrogenation

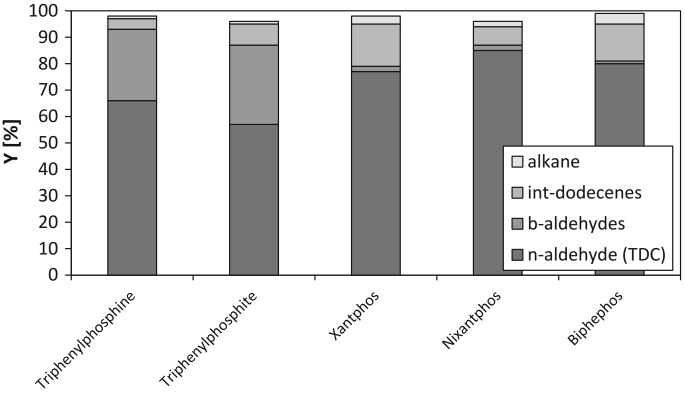

Fig. 11.3 Ligand screening. Conditions: (0.0068 mol 1-dodecene (1.14 g), $6.8 \cdot 10^{-6}$ mol Rh(acac)(CO)$_2$ (1.7 mg), $n_{\text{1-dodecene}}:n_{\text{Rh}}$ = 1000:1, $n_{\text{Rh}}:n_{\text{Ligand}}$ = 1:20, 8.5 ml toluene, 650 rpm, 20 bar CO:H$_2$ (1:1), 100 °C, 2 h)

most promising ligands for the hydroformylation of 1-dodecene, where triphenylphosphine (TPP) and triphenylphosphite represent monodentate ligands and Xantphos, Nixantphos, and Biphephos represent bidentate chelating ligands. Although the monodentate ligands lead to higher amounts of aldehydes (about 90%), the bidentate ligands seem to be more suitable for the aspired process featuring higher *n/iso*-ratios (about 99:1) combined with higher yields of the desired linear aldehyde *n*-tridecanal (about 80%).

In order to design a novel continuous process for the hydroformylation of 1-dodecene, it is not sufficient to focus on the final yield and the *n/iso*-ratio but also on the reaction rate. In respect to a holistic process development also the catalyst recovery has to be taken into account.

One approach of recycling the homogeneous catalyst complex is the use of a thermomorphic solvent system (TMS), where two phases are used to separate the product from the catalyst. In contrast to the RCh-RP-process, the phase behaviour of the reaction mixture can be switched by temperature changes. So that both the polar phase rich in catalyst and the apolar phase rich in substrate and product form a homogenous solution at reaction temperature. Furthermore, two phases can be recreated with lowering the temperature to separate the catalyst from the product again. Using this kind of solvent system, low catalyst leaching and a high concentration of the product in the apolar solvent can be achieved [7]. In the recent process development, the TMS-system containing the apolar solvent *n*-decane and the polar solvent DMF results in desired phase behaviour, good catalyst separation from the product, and high reaction rates. The optimal composition was found in 50 wt% *n*-decane and 50 wt% DMF [8].

Using this solvent system, the five ligands described before were compared in further reactions. In these investigations, the reaction is additionally observed during the whole time span by taking samples at certain points of time. Figure 11.4 shows the yield of the main product *n*-tridecanal over the time of 5 h.

Comparing the *n*-tridecanal yield for all the used ligands after five hours, Nixantphos shows the highest yield of *n*-tridecanal and therefore best results as found in the experiments before (compare Fig. 11.3). In respect to an industrial process also the time to reach the final yield has to be considered, leading directly to the residence time in the continuously operated reactor. Therefore, the steep slope of the reaction using the Biphephos ligand leads to the final *n*-tridecanal yield after 1 h, almost reaching the yield using Nixantphos. On the whole, Biphephos shows the best performance in the reaction comparing the *n*-tridecanal yield, the *n/iso*-ratio and the reaction rate.

Based on the selection of the catalyst complex and the used solvents, further reaction parameters such as reaction temperature, pressure, and synthesis gas composition have to be optimised. The best reaction performance was reached with

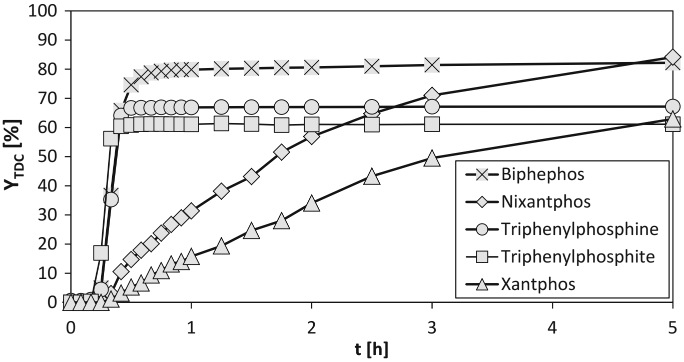

Fig. 11.4 Yield versus time plot considering most promising ligands. Conditions: (0.045 mol 1-dodecene (7.56 g), $4.5 \cdot 10^{-5}$ mol Rh(acac)(CO)$_2$ (11.6 mg), $n_{1\text{-dodecene}}:n_{\text{Rh}} = 1000:1$, $n_{\text{Rh}}:n_{\text{Ligand}} = 1:5$, 21.75 ml DMF (20.66 g), 28.25 ml *n*-decane (20.62 g), 800 rpm, 30 bar CO:H_2 (1:1), 100 °C

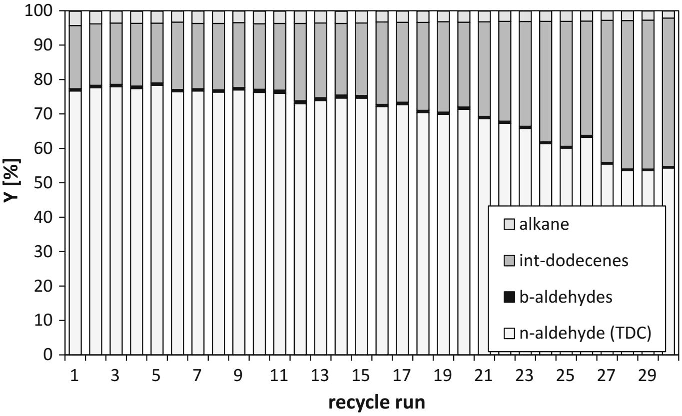

Fig. 11.5 Catalyst recycling in the TMS-system. Conditions: run1: 0.026 mol 1-dodecene (4.37 g), $2.6 \cdot 10^{-5}$ mol Rh(acac)(CO)$_2$ (6.7 mg), $n_{\text{1-dodecene}}$:n_{Rh} = 1000:1, n_{Rh}:$n_{\text{Biphephos}}$ = 1:20, 13.04 ml DMF (12.39 g), 16.96 ml *n*-decane (12.39 g), 800 rpm, 20 bar CO:H$_2$ (1:1), T_R = 100 °C, 1 h, T_S = −10 °C | run2–5: 0.026 mol 1-dodecene (4.37 g), $7.8 \cdot 10^{-5}$ mol Biphephos (61.4 mg), 1.30 ml DMF (1.24 g), 16.96 ml *n*-decane (12.39 g), 800 rpm, 20 bar CO:H$_2$ (1:1), T_R = 100 °C, 1 h, T_S = −10 °C | run6–30: 0.026 mol 1-dodecene (4.37 g), $7.8 \cdot 10^{-5}$ mol Biphephos (61.4 mg), DMF replenishment to 12.39 g, 16.96 ml *n*-decane (12.39 g), 800 rpm, 20 bar CO:H$_2$ (1:1), T_R = 100 °C, 1 h, T_S = −10 °C, run14–18: 1.25 h, run19: 1.6 h, run 20–25: 2 h, run 26: 2.25 h, run 27–30: 2 h

a synthesis gas pressure of 20 bar and a composition of 50 mol% H$_2$ and 50 mol% CO, a reaction temperature of 90–100 °C, and a stirrer speed of 800 rpm. Using these parameters, the reaction was carried out in a *Parr*-autoclave in a 40 g batch. After phase separation at −10 °C in a separation funnel, the catalyst phase was fed back to the reactor and used in another reaction run. In Fig. 11.5, the procedure of reaction, catalyst separation, and recycling was repeated 30 times (Fig. 11.5). In this reaction sequence, the high *n/iso*-ratio of 99:1 was reached in each run, although just a very low amount of Biphephos was replenished [4, 6].

The investigations shown in Figs. 11.4 and 11.5 lead to a determination of the residence time in a continuous reactor and prove the possibility to recycle the active catalyst complex. Although the recycling concept is proven in batch mode, these experiments are not sufficient for a scale up to build an industrial process. Therefore reaction rates, phase separation, and catalyst stability have to be investigated consecutively in a continuously operated miniplant [9].

11.3 Miniplant Process

Figure 11.6 shows the simplified flow sheet of the miniplant for further investigations on the hydroformylation of 1-dodecene in continuously operated mode. Therefore the two main apparatus and the inlet-, outlet-, and recycle streams are

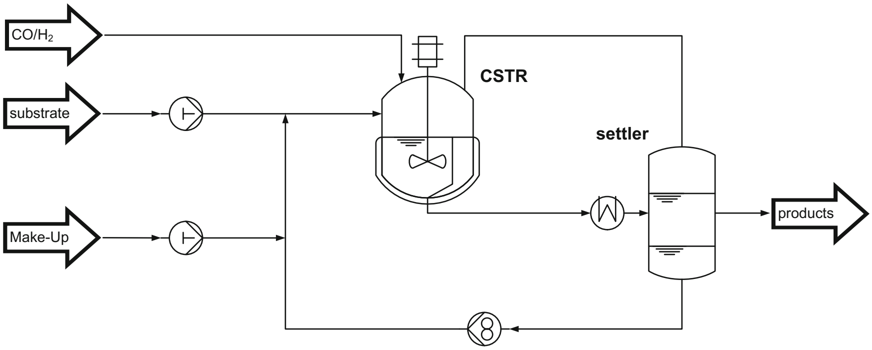

Fig. 11.6 Process flow sheet of the miniplant (CSTR and settler)

presented. The hydroformylation takes place in a 1000 ml *Büchi*-autoklave which is modified to operate as continuously stirred tank reactor (CSTR). After the reaction is carried out, the homogeneous mixture is transferred into the settler subsequently, where the two phases are separated from each other, on the one hand the apolar phase rich in product and on the other hand the polar phase rich in catalyst. The substrate 1-dodecene is fed by a piston pump combined with the apolar solvent *n*-decane into the CSTR. The catalyst solved in the polar solvent DMF is continuously circulated from the settler back to the reactor with a gear pump. The product *n*-tridecanal and the *n*-decane are removed out of the active process through an overflow pipe [10].

As shown in Fig. 11.4, the maximum yield of *n*-tridecanal is reached after 40–45 min. in batch experiments using the Biphephos ligand. This knowledge was transferred to the design of the CSTR so that a residence time of 41 min. was chosen. Therefore, the liquid feed stream was set to 60 ml (27.6 wt% 1-dodecene and 72.4 wt% *n*-decane) and a recycle stream of 380 ml/h to realise the calculated residence time was established. Conductivity measurements showed a real residence time of 39 min. [10].

For the phase separation, a settler with two concentric segments, which are separated trough a lead pipe from each other, is used. The liquid hold-up is adjusted with two overflow pipes, the lower one in the inner segment for the polar catalyst phase and the upper pipe in the outer segment for the apolar product phase. The separation principle of the used settler is shown in detail in Fig. 11.7 [10].

The polar catalyst phase is recirculated to the reactor with a volume flow of 380 ml/h as described before and the apolar product phase is removed from the process.

Both, the catalyst phase and the product phase are filled into the reactor to start the miniplant process. Therefore the total liquid hold-up of the miniplant and the desired composition of the liquids are used. The reactor is operated for 4 h in batch mode and then switched to continuous mode, where the reaction mixture leaves the reactor through an overflow pipe and enters the settler, to be separated into two

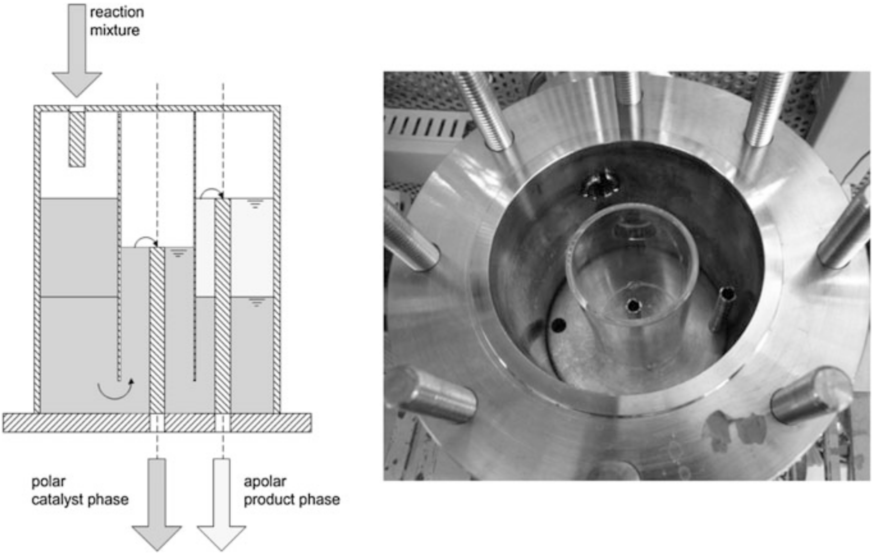

Fig. 11.7 Separation principle of the settler

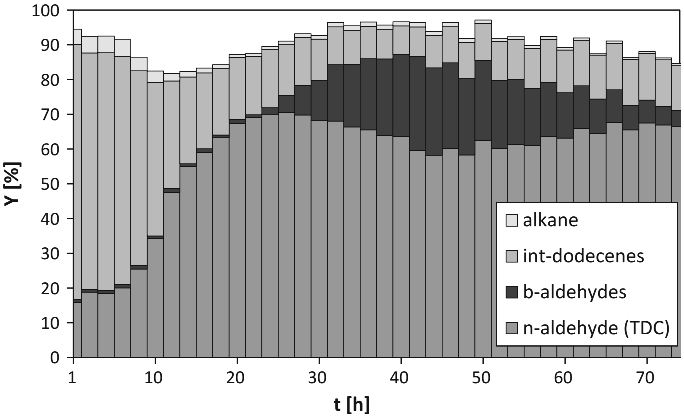

Fig. 11.8 First miniplant investigations. Conditions: $p = 20$ bar CO:H_2 (1:1), $T_R = 90$ °C, $T_S = 5$ °C, 750 rpm, $m_{\mathrm{DMF}} = 274.65$ g, $m_{\mathrm{Rh(acac)(CO)2}} = 0.0755$ g, $\dot{m}_{\mathrm{Biphephos}} = 1.1500$ g, $\dot{m}_{1-\mathrm{dodecene}} = 12.23$ g/h, $\dot{m}_{n-\mathrm{decane}} = 32.07$ g/h, *from 40 h: $\dot{m}_{\mathrm{Biphephos}} = 31$ mg/h

liquid phases. This step is defined as switching point from batch to continuous operation (and defined as 0 h in following diagrams). In Fig. 11.8, the yields at certain times are presented for the whole continuous operation [11].

During the first 20 h in continuous mode, the yield of the desired product TDC increases constantly and finally reaches about 70%. During this period of time, the same *n/iso*-ratio, compared to the batch investigations, is detected. After that, the overall yield in aldehydes still increases for another 20 h to reach the maximum of 87%. Meanwhile, the selectivity decreases and reaches a *n/iso*-ratio of 65:35. In order to recreate the desired *n/iso*-ratio small amounts of the Biphephos ligand is added to the process after 40 h constantly.

Several optimisations of the miniplant operation lead to steady-state miniplant runs which were carried out more than 200 h with high *n/iso*-ratio of 99:1 as predicted. Figure 11.9 shows the yields of the desired *n*-tridecanal, methyldodecanal, and the internal olefins. Since the start-up procedure is switched from batch mode at the beginning to continuous substrate supply, the start-up behaviour shown in Fig. 11.8 can be avoided. During the whole optimised miniplant run (Fig. 11.9), the Biphephos ligand has to be replenished in small amounts, to compensate ligand degradation and guarantee the high *n/iso*-ratio (99:1). Also, losses of the catalyst metal and the polar solvent have to be added continuously. These replenishments are served in a separate feed stream, shown in Fig. 11.6 as make-up stream [12].

Besides the optimisation of the process in terms of selectivity, start-up behaviour and long-term performance, the recovery of all solvents forming the TMS-system is of major interest. Therefore, the process presented in Fig. 11.6 can be extended by a thermal separation unit (e.g. distillation column) to separate the *n*-decane and unconverted olefins. The final process flow diagram is shown in Fig. 11.10. Here, the unpolar product phase leaving the phase separator is expanded at ambient pressure and buffered in a liquid hold-up. Subsequently the product mixture is fed to the distillation column, which is operated at an absolute pressure of 10 mbar. The recovered *n*-decane and olefins are buffered in a liquid hold-up again and fed back to the reactor [13].

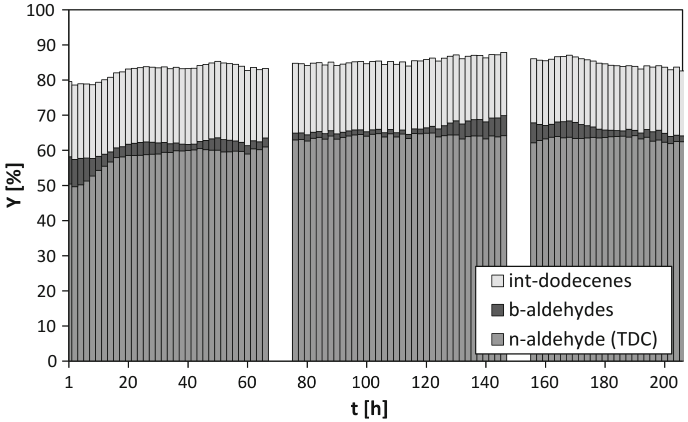

Fig. 11.9 Yields in the continuous miniplant process. Conditions: p = 20 bar CO:H$_2$ (1:1), T_R = 90 °C, T_S = 5 °C, 750 rpm, m_{DMF} = 274.65 g, $m_{\mathrm{Rh(acac)(CO)2}}$ = 0.0378 g, $m_{\mathrm{Biphephos}}$ = 0.5750 g, $\dot{m}_{1-\mathrm{dodecene}}$ = 12.23 g/h, $\dot{m}_{n-\mathrm{decane}}$ = 32.07 g/h, $\dot{m}_{\mathrm{DMF}}$ = 4.25 g/h, $\dot{m}_{\mathrm{Rh(acac)(CO)2}}$= 0.25 mg/h, $\dot{m}_{\mathrm{Biphephos}}$ = 31mg/h

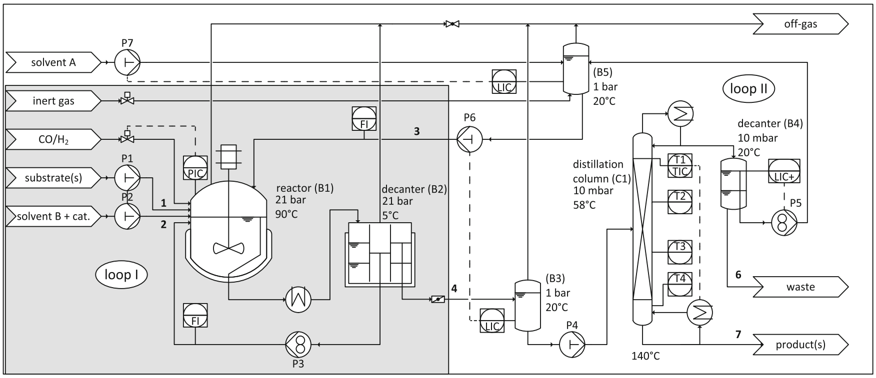

Fig. 11.10 Process flow diagram of the extended miniplant process for continuous hydroformylation

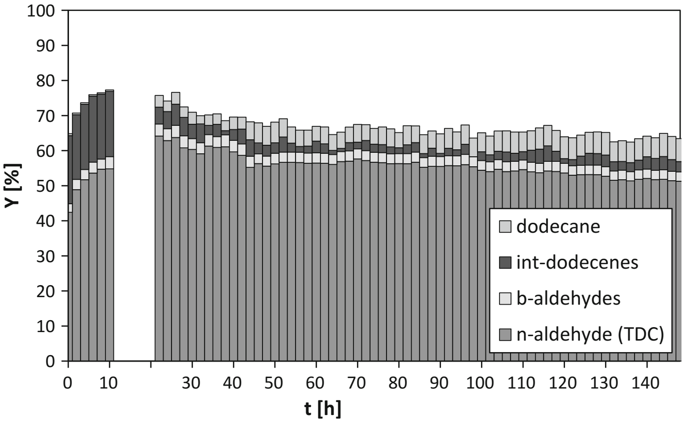

Fig. 11.11 Yields in the continuous miniplant process. Conditions: $p_{R,S}$ = 20 bar CO:H_2 (1:1), T_R = 90 °C, T_S = 5 °C, 750 rpm, m_{DMF} = 274.65 g, $m_{\mathrm{Rh(acac)(CO)2}}$ = 0.0378 g, $m_{\mathrm{Biphephos}}$ = 0.5750 g, $\dot{m}_{1-\mathrm{dodecene}}$ = 24.5 g/h, $\dot{m}_{\mathrm{DMF}}$ = 3 g/h, $\dot{m}_{\mathrm{Rh(acac)(CO)2}}$ = 0.25 mg/h, $\dot{m}_{\mathrm{Biphephos}}$ = 31 mg/h, $\dot{V}_{\mathrm{feed,column}}$ = 120 mL/h, p_{column} = 10 mbar, reflux ratio = 1

Figure 11.11 shows the yields of the continuous miniplant process presented in Fig. 11.10. During the start-up of the process, the obtained yields in the reactor are comparable to the previously presented operation. During this period, 1-dodecene and *n*-decane were fed to the reactor, so that the conditions only differ in the flow rate (1-dodecene + *n*-decane: Fig. 11.9 60 mL/h; Fig. 11.11 120 mL/h). Subsequently (10–20 h), the distillate stream of the distillation column was recycled to the reactor and feed streams were adjusted so that the ratio of olefins (1-dodecene + internal-olefins) and *n*-decane remained constant, still having a flow rate of 120 mL/h. After this start-up phase, the reaction behaviour was evaluated in the presented way (Fig. 11.11).

Due to the isomerisation and highly selective linear hydroformylation, the recycle of the internal olefins leads to a significant reduction of the isomerisation of the substrate 1-dodcene, from initially 15–3%. Over the course of investigation (20–150 h), the yield of the linear tridecanal decreases from 64 to 51%, while a *l*/*b*-ratio of 95/5 is preserved during the total operation. These results show the presence of the active catalyst species within the reactor, since the *l*/*b*-ratio does not change over time. Furthermore, the recycle of the internal olefins leads to the decrease of linear hydroformylation, since the combination of isomerisation and linear hydroformylation is slower than linear hydroformylation of the terminal olefin.

11.3.1 Hydroformylation of Renewables in a Continuous Process

The knowledge about the hydroformylation process of 1-dodecene in a miniplant using a thermomorphic solvent system served as background to develop a continuous process for the hydroformylation of renewables as shown in Fig. 11.1. Again highly selective linear hydroformylation is desired, while isomerisation of the double bond, hydroformylation to branched aldehydes and hydrogenation are side reactions (Fig. 11.12) [14].

Research by Ternel et al. on the hydroformylation of 10-undecennitril has shown that the known TMS-systems are not applicable for functionalising middle-polar substrates that already contain a polar functional group due to the high solubility of

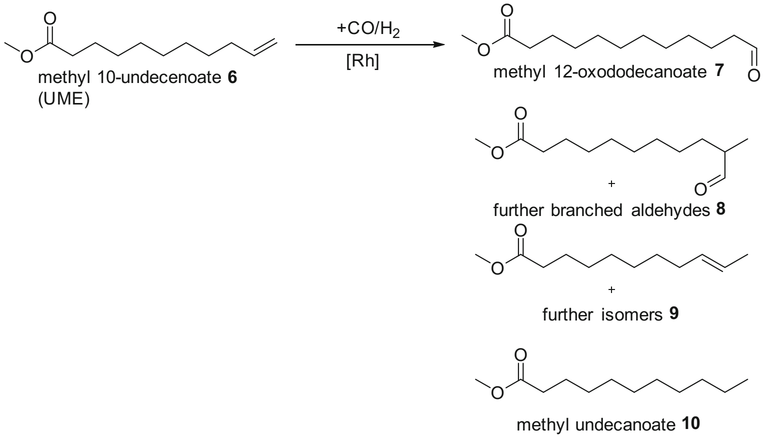

Fig. 11.12 Reaction scheme of the hydroformylation of methyl 10-undecenoate

the resulting products in the catalyst phase (>90%) [15]. With this in mind, again laboratory–scale research was conducted with the aim of developing a new concept that allows for both efficient process control with high yields and selectivities as well as easy catalyst recycling. Therefore, a so-called narrow-TMS-system consisting of the solvents water and 1-butanol was investigated. This solvent system shows the main criteria of a TMS-system, which are as follows:

- Low solubility of the product in the polar solvent
- High solubility of the catalyst complex in the polar solvent
- High temperature dependency of the miscibility gap

Although the reaction mixture consisting of water, 1-butanol and methyl 10-undecenoate does not form a single liquid phase at reaction temperature, high reaction rates were observed. Switching the polar solvent from DMF to water also needs for a replacement of the catalyst complex, due to low solubility of the Biphephos ligand in the aqueous phase. Therefore, the ligand SulfoXantphos was used. Figure 11.13 shows the yields of the obtained products at different temperatures. While the yields of the desired linear hydroformylation product increases from 18% at 120 °C to 79% at 150 °C, an improvement of mass transport between catalyst phase and substrate-product phase was detected. The subsequent decrease in selectivity and also hydroformylation activity can be explained by ligand decomposition at higher temperatures.

As described before, catalyst recovery and recycling were investigated in batch operation. Therefore, the liquid phases were separated in a separation funnel, the catalyst phase recycled back to the autoclave and fresh substrate was added.

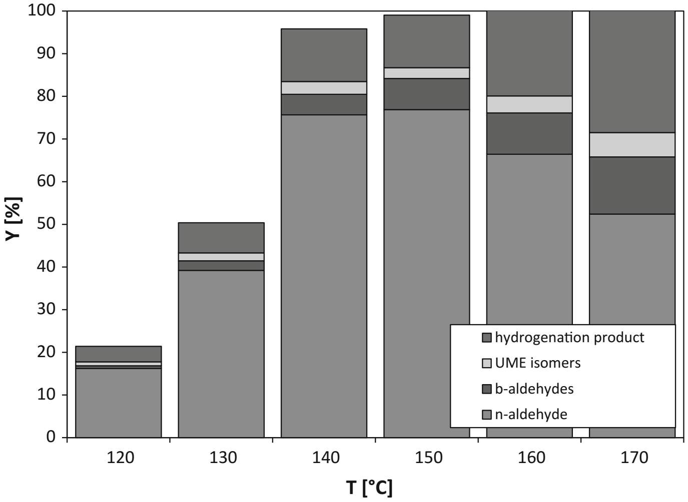

Fig. 11.13 Hydroformylation of methyl 10-undecenoate: Temperature screening. Conditions: 4 mmol UME, $n_{\mathrm{Rh}}:n_{\mathrm{UME}} = 1:2000$, $n_{\mathrm{Rh}}:n_{\mathrm{P}} = 1:10$, $p = 20$ bar, $\mathrm{CO:H_2} = 1:1$, $t = 1$ h, $m_{n\text{-butanol}} = 2{,}1$ g, $m_{\mathrm{H_2O}} = 2{,}1$ g, $\mathrm{Rh(acac)(CO)_2}$, SulfoXantphos

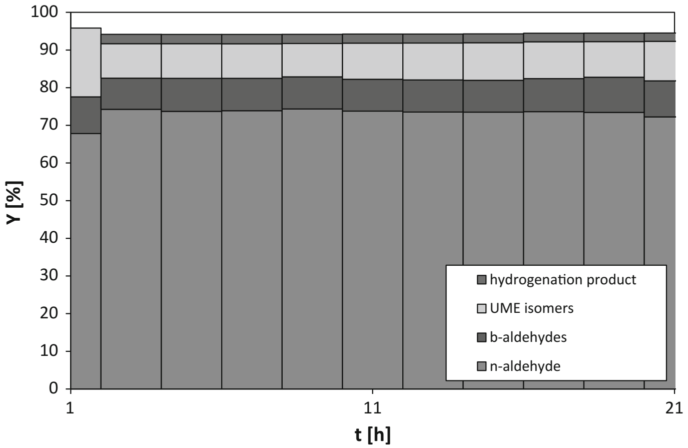

Fig. 11.14 Continuous hydroformylation of methyl 10-undecenoate in a miniplant. Conditions: $p = 20$ bar, CO:H_2 = 1:1, $T_R = 140$ °C, $T_S = 5$ °C, $w_{n\text{-butanol}}:w_{H2O} = 1:1$, $m_{H2O} = 300$ g, $m_{Rh(acac)(CO)2} = 0.071$ g, $m_{SulfoXantphos} = 1.071$ g, $\dot{V}_{UME} = 17.7$ ml/h, $\dot{V}_{n-\text{butanol}} = 42.3$ ml/h

Catalyst recovery was shown in three consecutive hydroformylation runs at 140 °C without any decrease in selectivity and activity and without catalyst or ligand replenishment. As the miniplant process shown in Fig. 11.6 was operated in a steady state for the hydroformylation of 1-dodecene, again this process was continuously operated for the hydroformylation of methyl 10-undecenoate. After the start-up procedure, continuous miniplant operation was achieved (Fig. 11.14). A constantly high yield of the linear product at 73% was achieved over the course of miniplant operation over 21 h. In terms of the reaction behaviour of the CSTR, virtually the same selectivity was observed compared to prior experiments in the batch autoclave. Only the rhodium concentration of 15 weight-ppm in the product stream under continuous operation is higher compared to the batch separation. As the water phase decreased under continuous operation owing to its solubility in 1-butanol, catalyst leaching was likely favoured. Nevertheless, stable process conditions were maintained for 21 h without interference, which demonstrates the stability of the catalyst species under process conditions.

11.4 Conclusions

Herein, the process development for the hydroformylation of the long chained olefin 1-dodecene was shown. Based on the selection of a suitable transition metal catalyst complex, the reaction behaviour was investigated extensively. Afterwards the catalyst recycling concept of thermomophic solvent systems was introduced. A TMS-system consisting of DMF and *n*-decane was used for catalyst recycling in batch mode. Following the experience, a miniplant process was designed and investigations on long-term behaviour were conducted in continuous operation, which finally resulted in steady-state operation and the recycling of the catalyst as well as all of the used solvents.

This knowledge was transferred to the hydroformylation of the renewable resource methyl 10-undecenoate. Having main criteria of process development based on TMS-systems in mind, again the hydroformylation reaction was characterised and the catalyst recycled in batch operation. For this, a narrow-TMS-system consisting of water and 1-butanol was introduced. In the end, stable miniplant operation was shown for 20 h.

TMS-systems are promising for continuous hydroformylation processes of long chained olefins and renewable resources. With this catalyst recycling technique also high catalyst activity can be preserved, so that reaction and separation can be operated continuously. But still several points for optimisation of this concept remain, e.g. increase of operation time, improvement of catalyst separation, or variation of substrates like methyl oleate.

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Chapter 12
Future Developments in Homogenous Catalysis with Renewables

Arno Behr and Andreas J. Vorholt

In this book, several recent developments for the usage of renewables with homogeneous catalysis are presented. At the present stage of development, classic homogeneous catalysed reactions, such as hydrogenation, metathesis, hydroformylation, telomerisation, aminations, or oxidations, play a key role.

Specially, the hydrogenation of CO_2 for energy storage is an emerging field and is promising especially if it comes to rechargeable systems. Hydrogenations are further a tool to tailor-made product mixtures from crude renewable polymers like celluloses or lignin. The topic of cracking the natural polymers to smaller platform molecules will be a field in the future where homogeneous catalysis can give high regioselectivity towards certain bond cleavage in, e.g., lignin. Therefore, further developments for more tolerant catalyst against impurities and the recycling or separation of the catalyst are of high need.

Also, in the work-up of crude renewable mixtures, the oxidation is a very potent tool to generate small intermediates. This field is not so far developed than the hydrogenation, so new ideas on catalyst systems with high selectivities will play a role for this reaction and if these conversions will be applied in bigger scales. Furthermore, oxidation of fatty compounds delivers today industrially monomers and other everyday chemicals. The development of catalysed processes to get rid of the energy-intensive ozonolysis is still ongoing. Here, the development of recycling techniques for the homogeneous catalyst is crucial for future applications. The oxidation with homogenous catalysis is a tool in the fine chemistry with, e.g., terpenes to yield very valuable products from renewable feedstocks.

Telomerisation, aminations, and hydroformylation are reactions to give renewables new or other functionalities. Telomerisations need conjugated double bonds, aminations a double bond or an alcohol moiety, and the hydroformylation a double bond to high value products. Telomerisations give a straightforward reaction to incorporate renewable nucleophiles or renewable terpenes which contain a conjugated double bond. The scope of the reaction with renewables is by far not explored, so there is room for new surfactants, or monomers by this reaction. The same is true for aminations, in which several renewable amines or renewable

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alcohols will play a role in the future. Hydroformylation is a very versatile reaction to yield aldehydes which are then intermediate, for example alcohols and amines. Fatty compounds or terpenes yield very interesting molecules for several intermediates. Therefore, we will see new applications of these reactions in future.

Hydroformylation is also a key step in several tandem reactions with renewables, besides isomerization, metathesis, and decomposition reactions. The merger of several reactions to convert renewables is very beneficial because no intermediate work-up is necessary to perform a variety of reaction steps to tailor-made products. So isomerization and metathesis of unsaturated fatty compounds can form a broad mixture of unsaturated fatty acids, alkenes, and diacids. Also, decomposition of, e.g., glycerol to syngas and their use in hydroformylation are a nice example where homogeneous catalysis can guide new directions. The isomerization and carbonylations of fatty acids are clearly one hot topic of the tandem reaction development over the last years and form directly from renewables monomers. These cases show the potential of tandem reactions, and more creative mergers of homogenous catalyst will be seen in the future.

All shown reactions of renewables catalysed by homogenous catalyst can only become economic if the precious catalyst can be separated or in the best case recycled. In this book, several recycle strategies are shown such as ionic liquids, supercritical CO_2, and thermomorphic systems. These approaches are the key to apply these techniques in a bigger scale. Therefore, miniplant or pilot plants are important to test the long-term stability of catalysts. In terms of stability operation times of several hundred to several thousand hours are indicators that processes can be run stable and are economical feasible. In particular, these aspects are under-represented in the today's academic research. Not only with renewables mechanisms for ligand degradation are unknown, so very nice transformations of substrates are at this stage just feasible for one batch reaction. In situ spectroscopy can give more information of the degradation mechanisms and has a big potential to enhance homogenously catalysed reactions.

To sum up, this book give an overview on homogeneously catalysed key reactions with renewables. A lot of reactions have been studied, but there is a big potential to find new substrates of the existing reactions or find new mergers of reactions. The development of the existing reactions to scalable processes and a combined recycling of the homogeneous catalyst are still an underestimated challenge that should be focused on future development more firmly.

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