

Chapter 7

Tandem Reactions with Renewables

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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

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

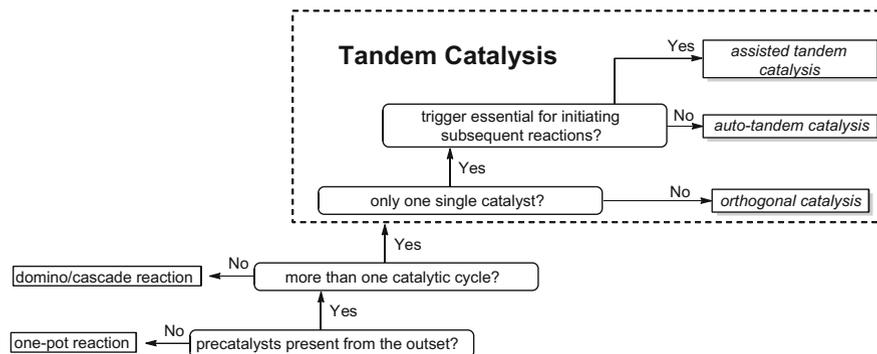


Fig. 7.1 Classification of tandem catalytic systems in the context of sequential transformations [14]

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 C₁₂-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

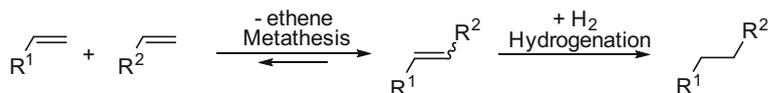


Fig. 7.2 General metathesis/hydrogenation of terminal olefins releasing ethene

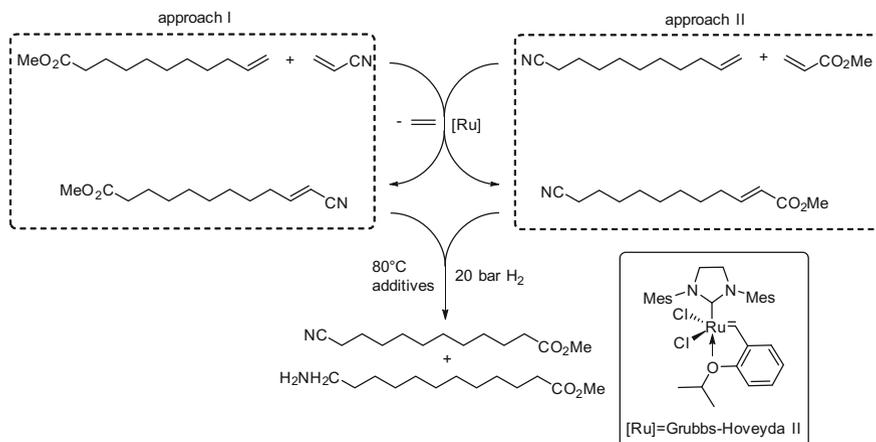


Fig. 7.3 Two approaches to saturated C₁₂-amine-esters by tandem catalysis with different substrates

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 C₁₂-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 ^tBuOK 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 C₂₀ unsaturated α,ω -dialdehydes in a self-metathesis reaction or, if acrolein is applied, C₁₁ 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

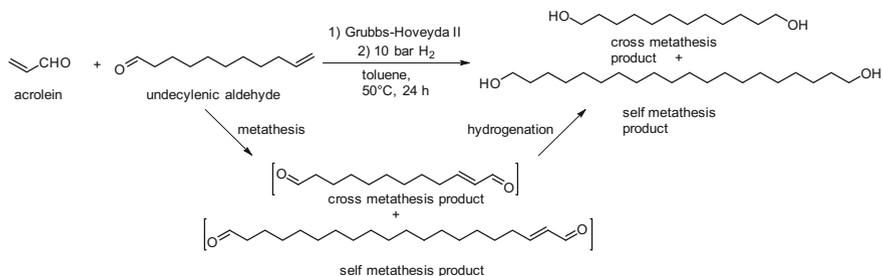


Fig. 7.4 Acrolein in a metathesis/hydrogenation tandem catalysis

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 transference 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].

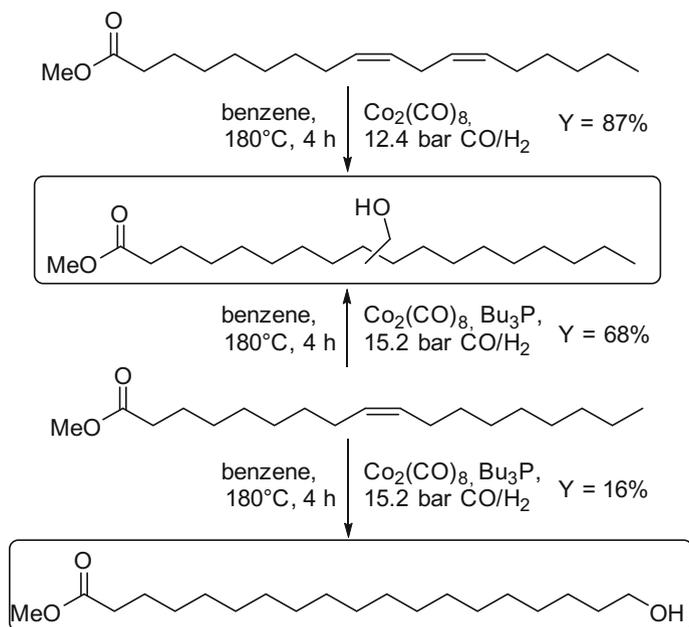


Fig. 7.6 Methyl linoleate and methyl oleate in tandem catalysis yielding alcohols

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, $\text{CO}_2(\text{CO})_8$ 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

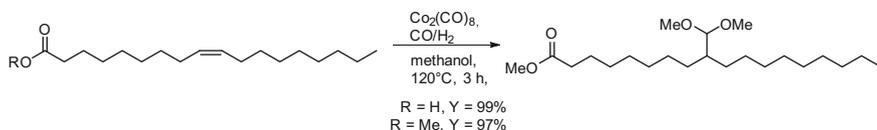


Fig. 7.7 Hydroformylation of oleic acid with subsequent acetalisation in a tandem catalysis

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 $P(O-o^t\text{BuPh})_3$ 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].

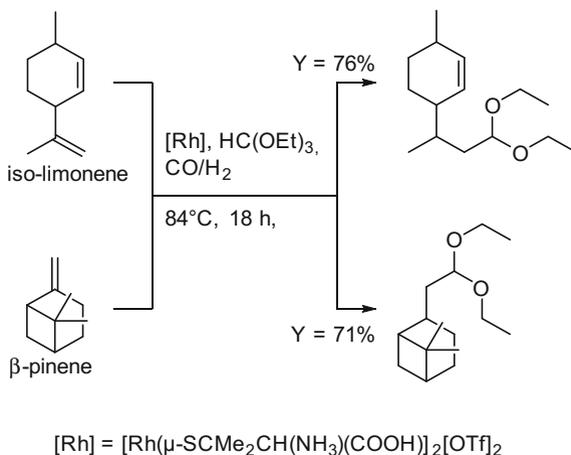


Fig. 7.8 Applying *iso*-limonene and β -pinene in hydroformylation/acetalisation

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 $[\text{Rh}(\mu\text{-S}^t\text{Bu})(\text{CO})(\text{P}(\text{OPh})_3)_2]$ 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

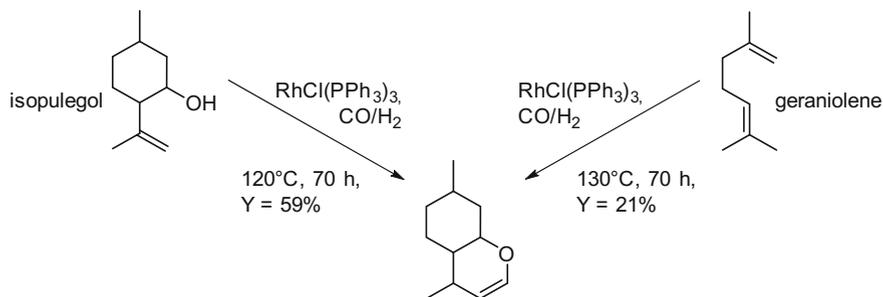


Fig. 7.9 Tandem catalytic approaches from isopulegol and geraniolene to a cyclic vinyl ether product

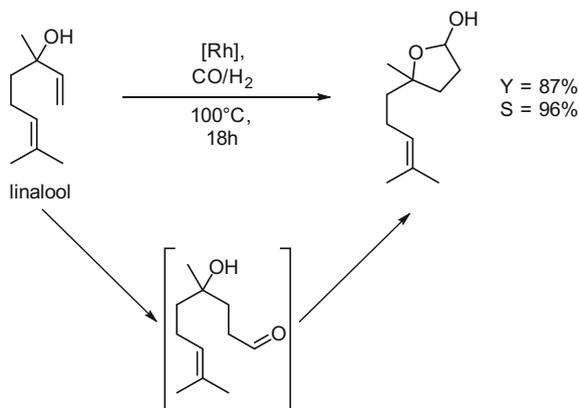


Fig. 7.10 Hydroformylation/lactolisation of linalool

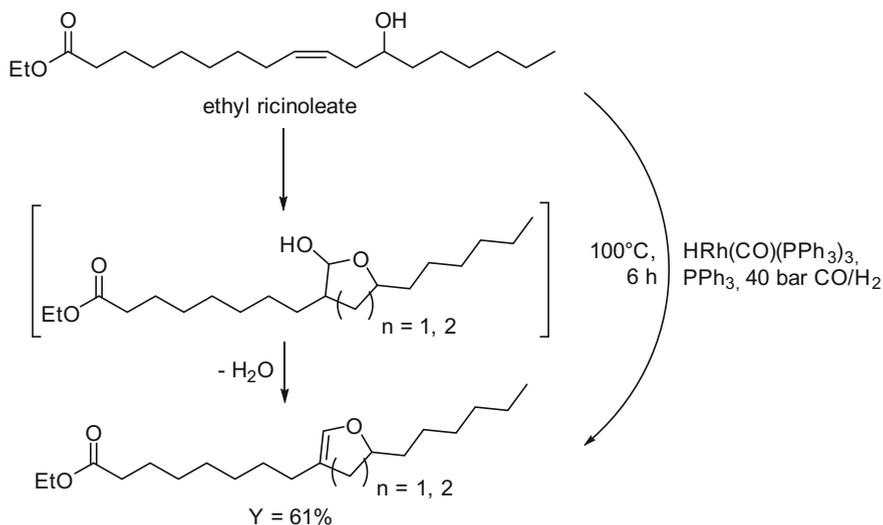


Fig. 7.11 Furanisation/pyranisation of ethyl ricinoleate in a tandem reaction under hydroformylation conditions

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 derivatives by hydroformylation, lactolisation, and condensation with yields for cyclic ethers of up to 61% for ethyl ricinoleate 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 $\text{PtCl}_2(\text{DPPB})$ (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

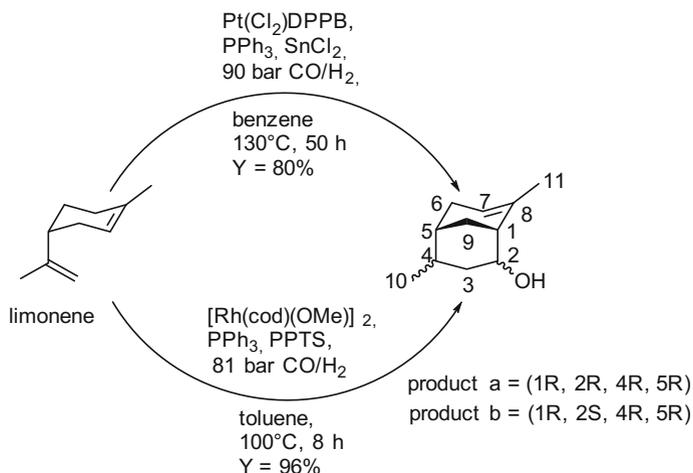


Fig. 7.12 Different approaches from limonene to a fragrance with high stereoselectivity

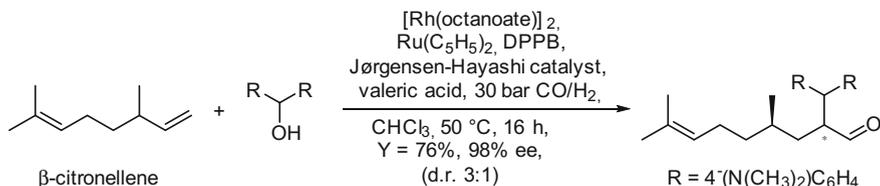
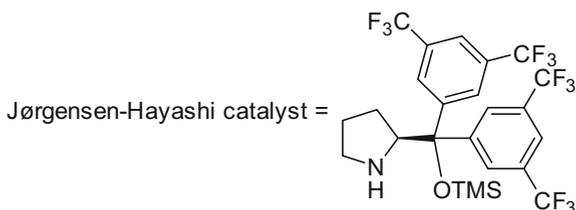


Fig. 7.13 Highly enantioselective tandem hydroformylation/alkylation of β -citronellene

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: $\text{Rh}(\text{CO})_2(\text{acac})$ with NAPHOS (=2,2' bis((diphenylphosphino)methyl)-1,1'-binaphthyl)) for the hydroformylation of citronellene, and the organocatalytic part: pyrrolidine with benzoic

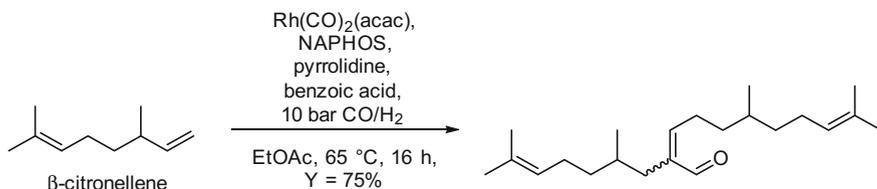


Fig. 7.15 Gaining α,β -unsaturated aldehydes in the tandem hydroformylation/aldol condensation

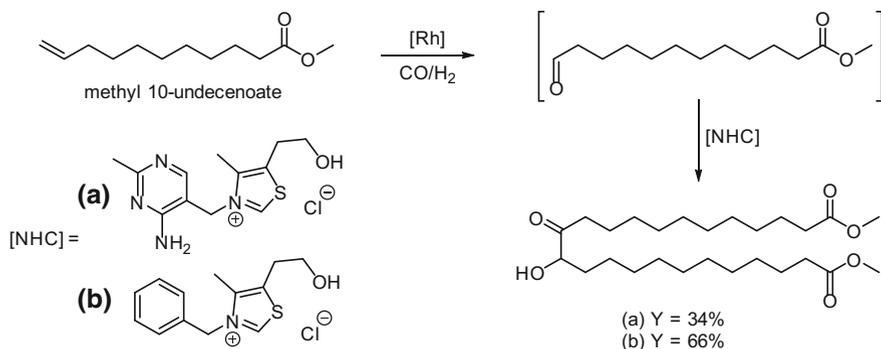


Fig. 7.16 Hydroformylation/acyloin reaction tandem catalysis with methyl 10-undecenoate for diester synthesis; **a** [Rh] = [Rh(acac)(CO)₂]/Biphephos, NHC = Vitamin B₁/Et₃N; **b** [Rh] = [Rh(acac)(CO)₂]/NiXantphos, NHC = more stable thiamine derivative

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

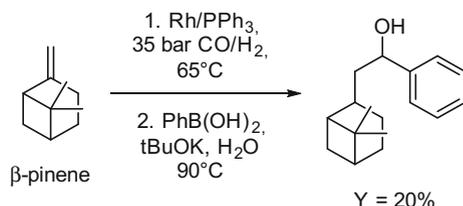
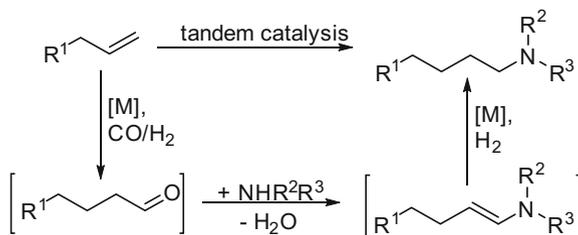


Fig. 7.18 Reaction pathway of the hydroaminomethylation with a secondary amine



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

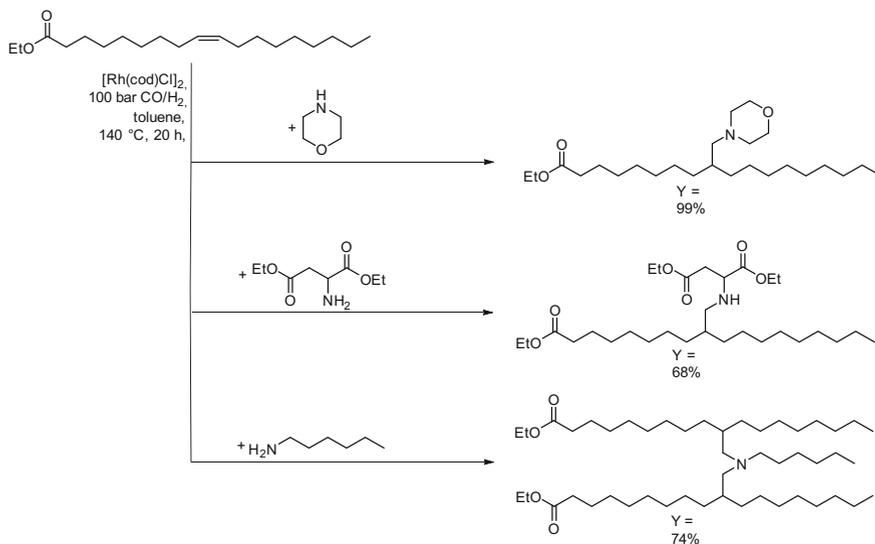


Fig. 7.19 Hydroaminomethylation of ethyl oleate with different amines

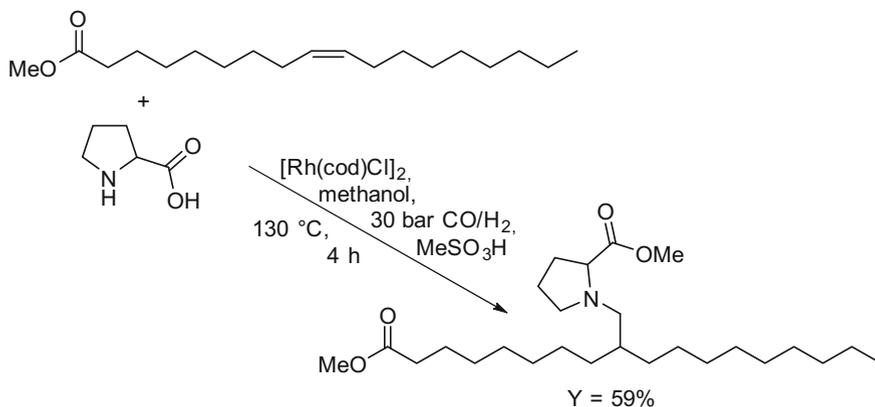


Fig. 7.20 Hydroaminomethylation of methyl oleate with proline

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

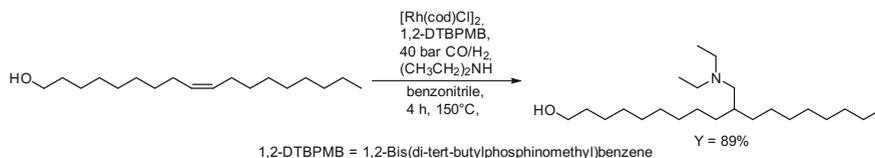


Fig. 7.21 Hydroaminomethylation of oleyl alcohol with diethylamine

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.

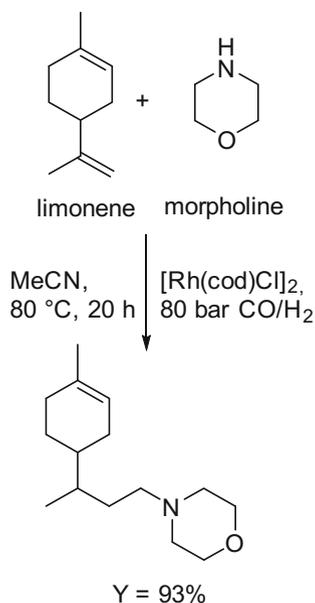


Fig. 7.22 Hydroaminomethylation of limonene with morpholine

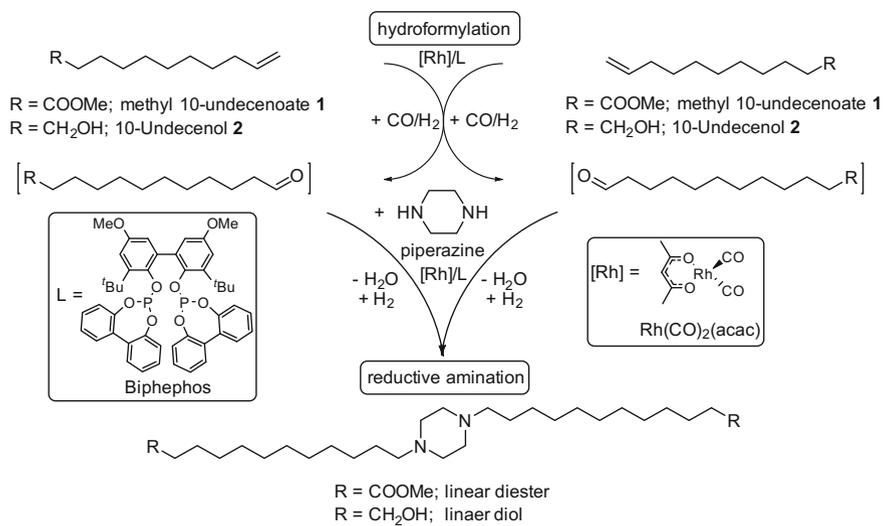


Fig. 7.23 Bis-Hydroaminomethylation of methyl 10-undecenoate and 10-undecenol with piperazine for the formation of a linear diester and a linear diol, respectively (Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission)

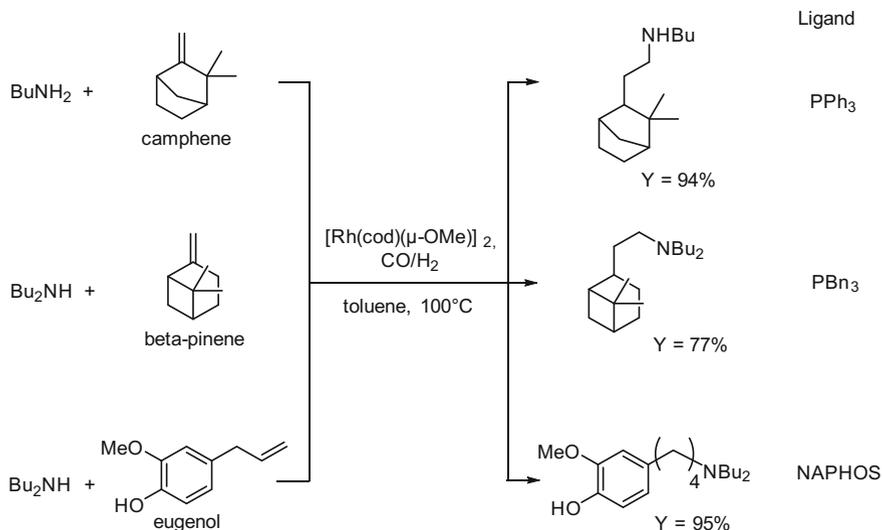


Fig. 7.24 Various terpenes and eugenol in hydroaminomethylation

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((diphenylphosphino)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).

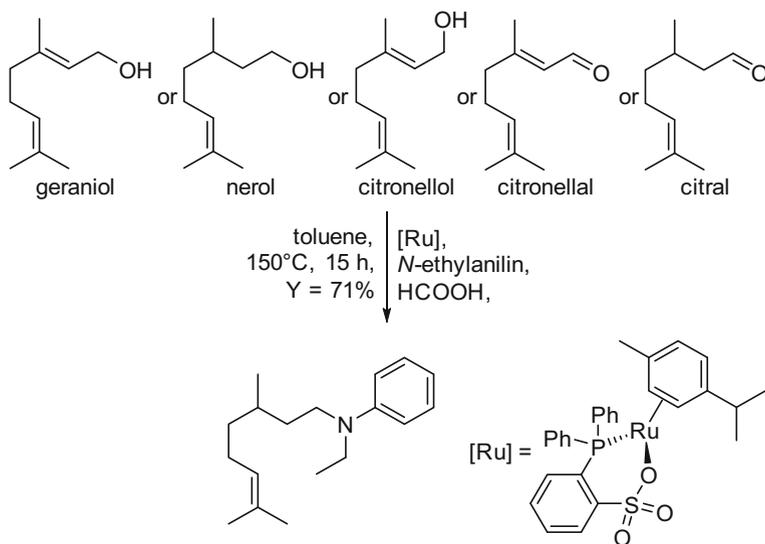


Fig. 7.25 Different starting molecules leading to the same compound by multiple tandem catalytic steps

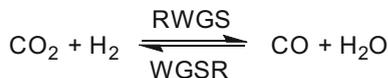
7.3.5 Alternative Syngas Resources for Hydroformylation

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 (WGS) 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 WGS



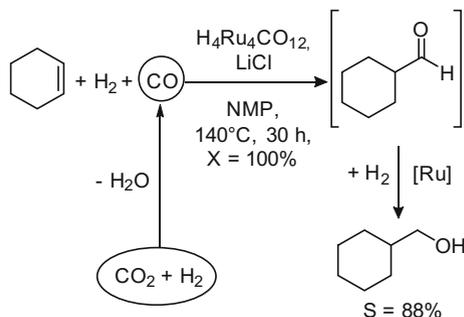


Fig. 7.27 Ruthenium-catalysed RWGS-reaction in tandem catalysis

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/H₂) due to less toxicity of carbon dioxide compared to carbon monoxide [99].

The catalyst system based on the complex H₄Ru₄CO₁₂ 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

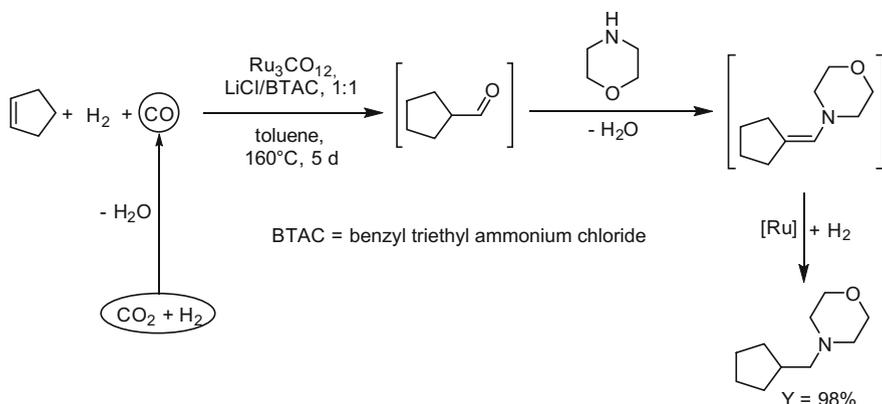


Fig. 7.28 Application of the RWGS in the hydroaminomethylation of cyclopentene with morpholine

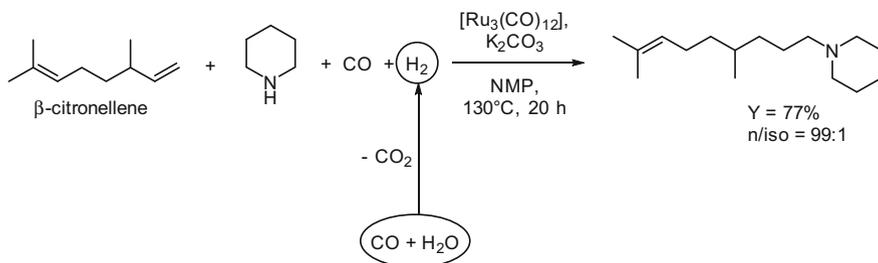


Fig. 7.29 Application of the WGS in the ruthenium-catalysed hydroaminomethylation of β -citronellene

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 WGS, 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 regioselectivities 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

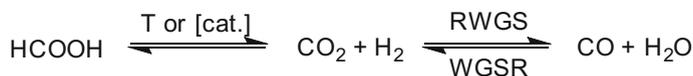


Fig. 7.30 Decomposition of formic acid leading to a RWGS

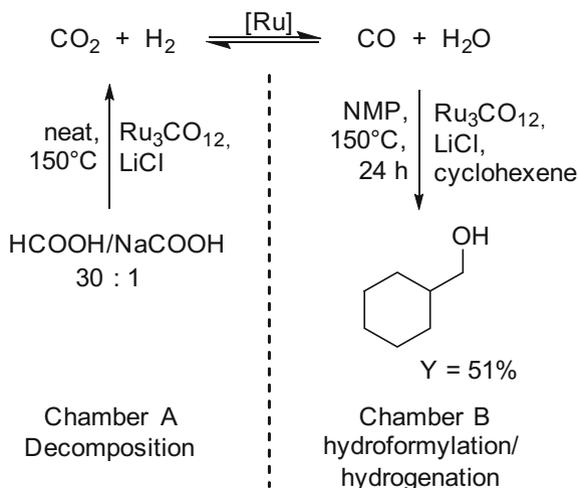


Fig. 7.31 Decomposition of formic acid and subsequent hydroformylation/hydrogenation in one tandem catalysis

acid as a CO₂ 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 CO₂ and H₂. The tandem catalysis consists of the decomposition of formic acid to CO₂ and H₂, 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 polyols, 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 $[\text{Ir}(\text{cod})\text{Cl}]_2$ and (*S*)-(-)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl ((*S*)-BINAP).

Fig. 7.32 Generating syngas from glycerol

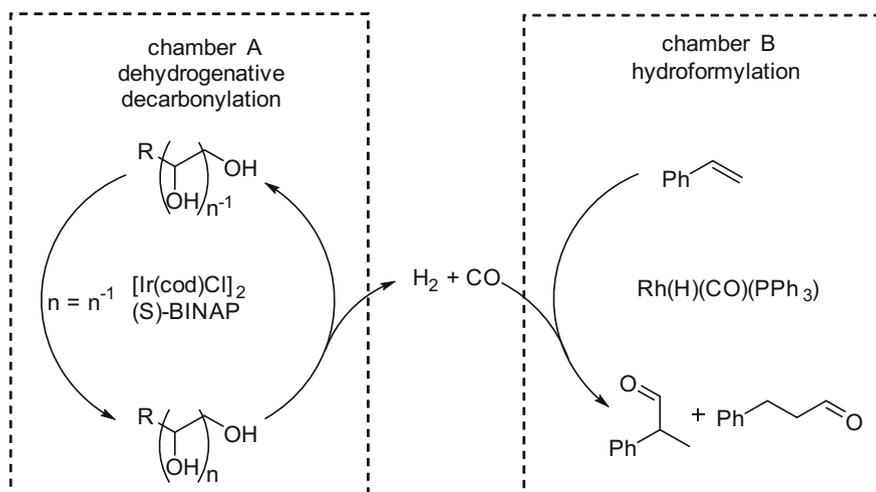


Fig. 7.33 Selective transfer of syngas from different polyols to styrene

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

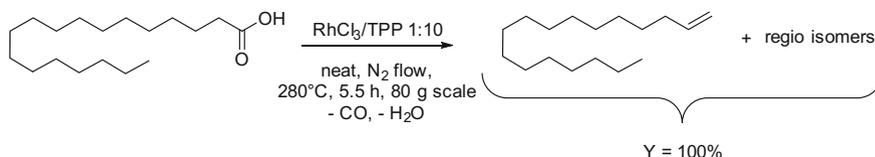


Fig. 7.34 Decarbonylative dehydration of stearic acid to heptadecenes

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 distilling the α -olefin from the autoclave to avoid side reactions [108]. A palladium system consisting of [Pd (TPP)₂Cl₂] 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 PdCl₂ 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. C₁₂, C₁₆, C₂₂ 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

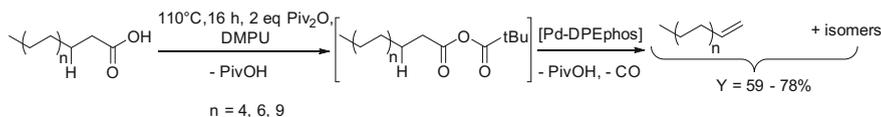


Fig. 7.35 Catalytic decarbonylative dehydration reaction of saturated fatty acids

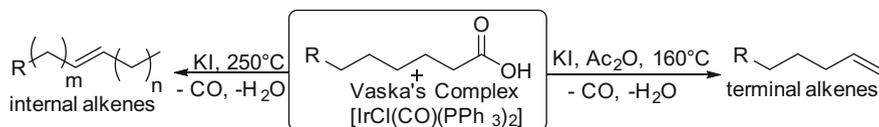


Fig. 7.36 Iridium-catalysed decarbonylative dehydration of aliphatic carboxylic acids to internal and terminal alkenes

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 $[\text{IrCl}(\text{CO})(\text{TPP})_2]$ 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% FeCl₂ 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 from stearic acid after 3 h is 74% (97/3 ratio of terminal to internal isomers). The reactions have to be conducted under a pressure of CO (20 atm) to assure iron-carbonyl complex formation. Fatty acids of different chain length from C₁₄ to C₂₂ 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 PdCl₂ and TPP as ligand under a flow of nitrogen. By switching the ligand from TPP to Xantphos 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 from the reaction mixture into a cooled receiving flask is performed [116].

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

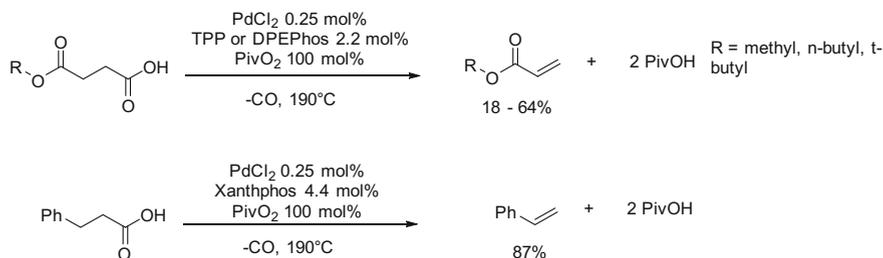


Fig. 7.37 Decarbonylative dehydrogenation of renewable mono-alkyl succinates and hydrocinnamic acid



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

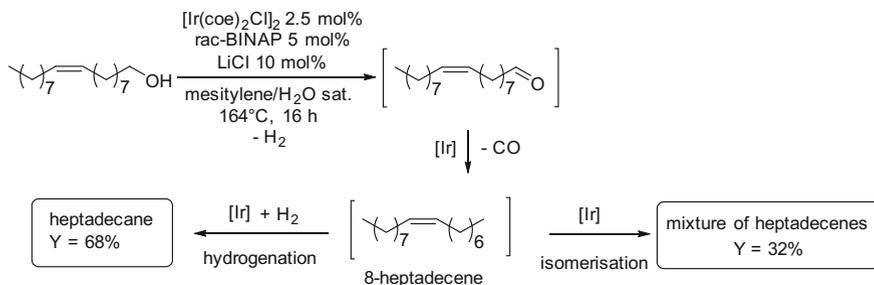


Fig. 7.39 Dehydrogenation/decarbonylation/hydrogenation sequence of oleyl alcohol

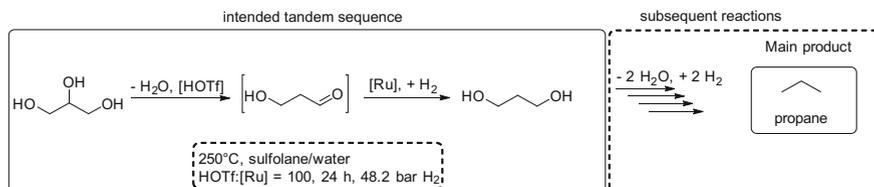


Fig. 7.40 Intended reaction from glycerol to 1,3-propanediol and subsequent reactions

ruthenium-catalysed hydrogenation to yield a selective, orthogonal tandem catalytic system. Triflic acid (HOTf) serves as a dehydration agent, yielding 3-hydroxypropanal, 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 , $[\text{HOTf}]:[\text{Ru}] = 100$, 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% $[\text{Ir}(\text{coe})_2\text{Cl}_2]$ 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.

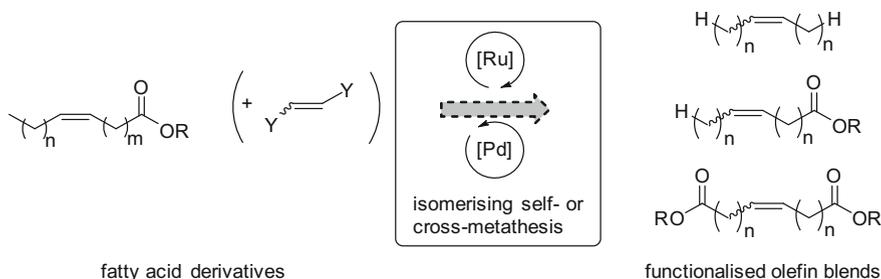


Fig. 7.41 Isomerising metathesis of unsaturated fatty esters with a ruthenium/palladium orthogonal tandem catalytic system

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 $[\text{Pd}(\mu\text{-Br})\text{Bu}_3\text{P}]_2$ 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 from 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 (CNSL), 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

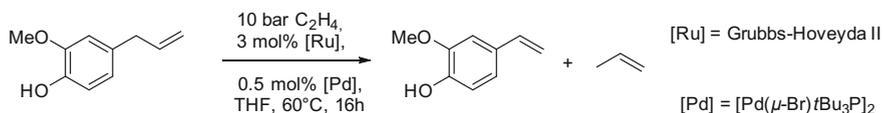
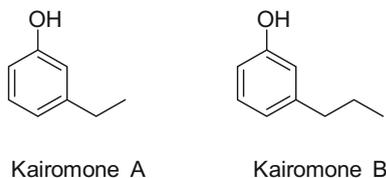


Fig. 7.42 Isomerising ethenolysis of eugenol

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 ([Pd(μ -Br) t Bu₃P]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

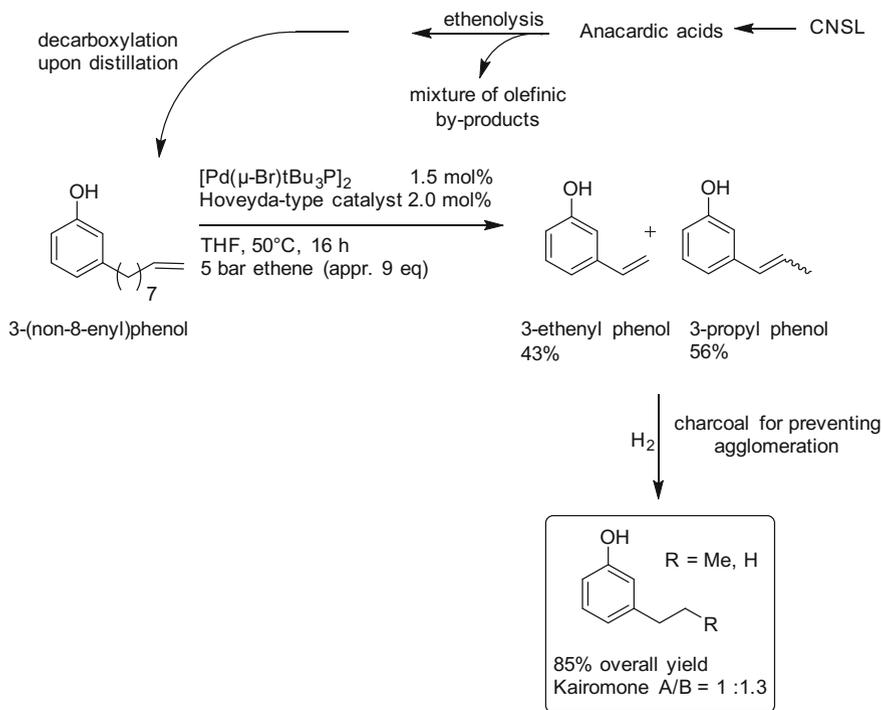


Fig. 7.44 Isomerising ethenolysis and hydrogenation in tandem catalysis as the key steps in the synthesis of tsetse fly attractants from renewable cashew nut shell liquid (CNSL)

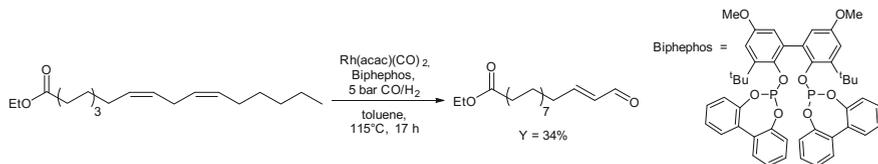


Fig. 7.45 Isomerising hydroformylation of linoleic ethyl ester

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

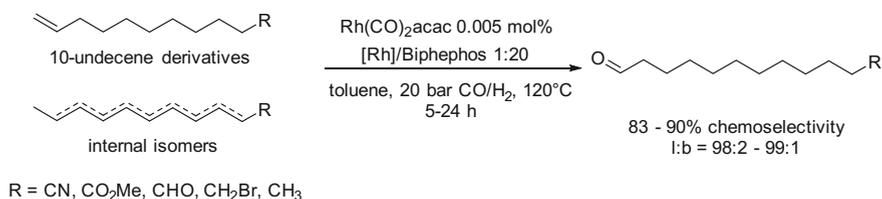


Fig. 7.46 Hydroformylation of 10-undecylenic derivatives including isomerising hydroformylation of internal isomers

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 $\text{Ru}_3\text{CO}_{12}$ 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

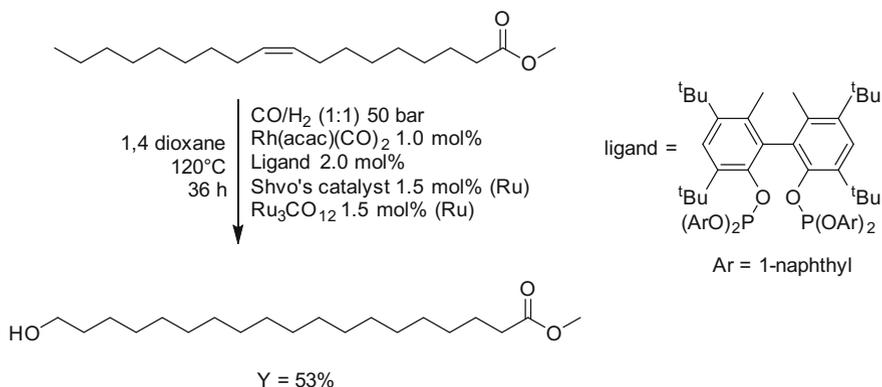


Fig. 7.47 Tandem catalysis of isomerisation, hydroformylation and hydrogenation of methyl oleate

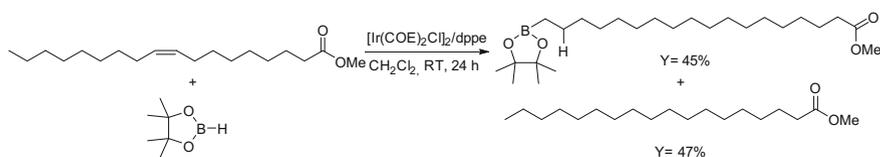


Fig. 7.48 Isomerising hydroboration of methyl oleate with pinacolborane

system for isomerising hydroboration with pinacolborane represents an auto-tandem catalytic system. At room temperature after 24 h, a catalyst derived from the precursor $[\text{Ir}(\text{COD})_2\text{Cl}]_2$ 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 $\text{BH}_3 \cdot \text{THF}$) 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

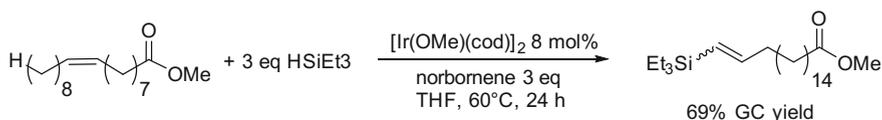


Fig. 7.49 Isomerising trialkylsilylation of methyl oleate to yield the terminal vinylsilane

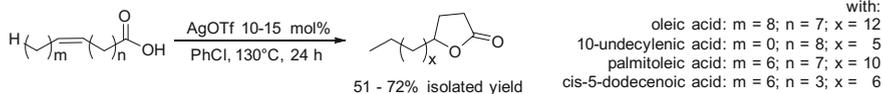


Fig. 7.50 Silver triflate catalysed isomerising lactonisation of fatty acids to corresponding five-ring lactones

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/ZnCl₂ 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

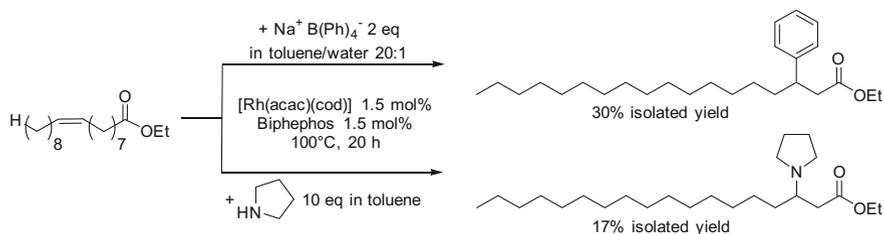


Fig. 7.51 Isomerisation/ β -functionalisation of ethyl oleate in tandem catalysis

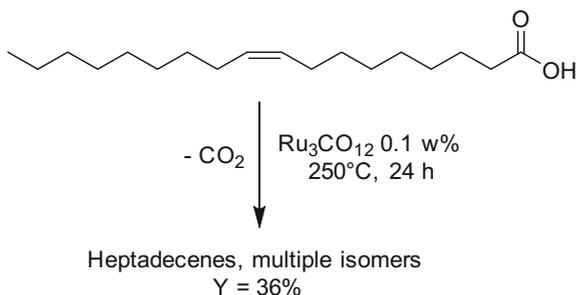
ethyl oleate. The Michael reaction in general is not limited to aminations and arylations, hence representing a flexible tool for β -functionalisations of fatty esters.

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 $[\text{Ru}(\text{CO})_2(\text{EtCO}_2)]_n$ 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 $[\text{RuCl}_2(\eta^3:\eta^2:\eta^3\text{-C}_{12}\text{H}_{18})_2]$ is most active, yielding 93–99% citronellol after 24 h at a low concentration of 1 mol%. ($\text{C}_{12}\text{H}_{18}$ = dodeca-2,6,10-triene-1,12-diy).

7.5.9 Isomerising Alkoxy-carbonylations

One of the most investigated and highly selective possibilities to introduce functionalities in the ω -position of the carbon chain of unsaturated fatty acid methyl esters are isomerising alkoxy-carbonylations. 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

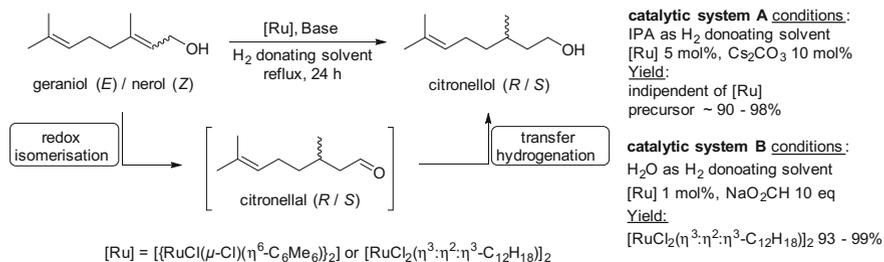


Fig. 7.53 Isomerising transfer hydrogenation of allylic alcohol moieties in terpenoids

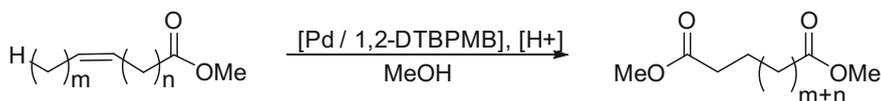


Fig. 7.54 Isomerising methoxycarbonylation of an unsaturated fatty acid methyl ester to yield the linear diester

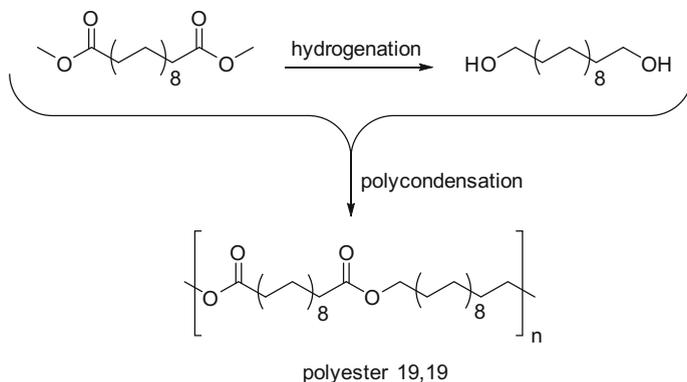
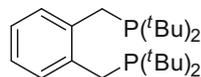


Fig. 7.55 Polycondensation of C19-diester from methoxycarbonylation of methyl oleate with the corresponding diester derived from hydrogenation

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 alkoxy carbonylation. 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 alkoxy carbonylations 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-Rodríguez 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 alkoxy carbonylation with this system.

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



The first example of diester synthesis from 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 C₁₉-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 those 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 alkoxy carbonylation 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 C₁₉-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 C₁₉-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 C₁₉-diester as a platform intermediate in renewable monomer production for potential polycondensates. C₁₉-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 C₁₉-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 methanesulphonic 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 C₁₉-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].

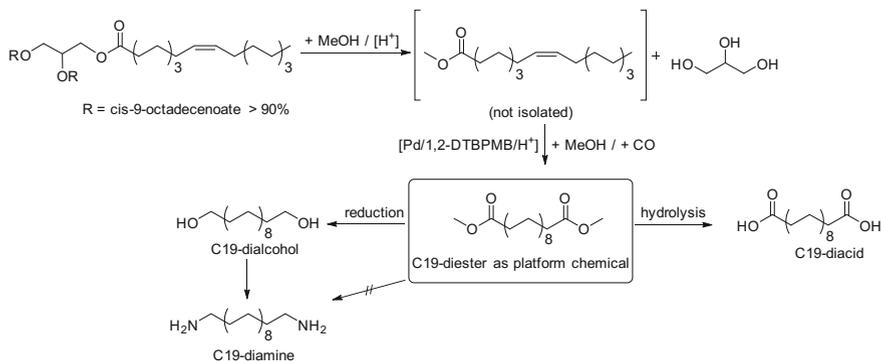


Fig. 7.57 Tandem reaction sequence leading from, e.g. HOSO to dimethyl 1,19-nonadecanedioate and polymer precursors derived thereof

Even more selective adamantyl-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 -bifunctional molecules from oleo chemicals [172].

The recycling of an auto-tandem catalytic system involving $\text{Pd}(\text{hfacac})_2$ 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 alkoxy carbonylation 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 alkoxy carbonylation 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.

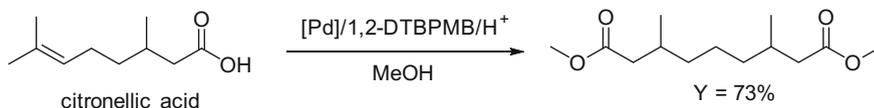


Fig. 7.58 Isomerising alkoxy-carbonylation of citronellic acid yielding a diester

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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