

# Chapter 6

## Oxidation of Renewables

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### 6.1 Introduction

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

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

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

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

**Table 6.1** Traditional oxidants and their E-factors

Oxidant	Oxygen generation reaction (mol O <sub>2</sub> /mol oxidant)	E-factor
Potassium bichromate	$\text{K}_2\text{Cr}_2\text{O}_7 + 4 \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + 4 \text{H}_2\text{O} + \mathbf{1.5 \text{ O}_2}$	13.3
Sodium hypochlorite	$\text{NaOCl} \rightarrow \text{NaCl} + \mathbf{0.5 \text{ O}_2}$	3.65
Chromic acid	$2 \text{CrO}_3 \rightarrow \text{Cr}_2\text{O}_3 + \mathbf{1.5 \text{ O}_2}$	3.17
Hydrogen peroxide	$\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \mathbf{0.5 \text{ O}_2}$	1.13
Ozone	$\text{O}_3 \rightarrow \mathbf{1.5 \text{ O}_2}$	0

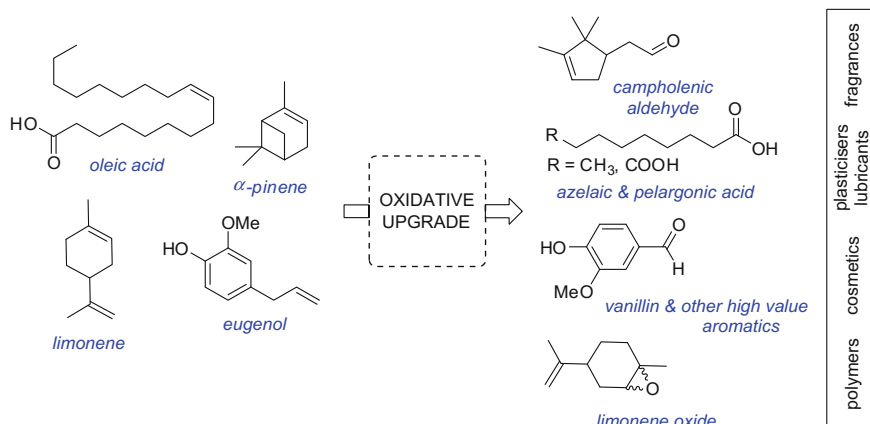
E-factor = mass waste/mass oxygen

no pollution potential or environmental risk, molecular oxygen is considered as the ideal reagent. In particular for the activation of O<sub>2</sub> and its selective introduction into molecules, the use of metal complexes is mandatory [8]. Moreover, often only one of the two oxygen atoms is transferred to the substrate to give the oxidised molecule. To avoid extra amounts of reducing agents, methods using both oxygen atoms are currently under investigation. Regarding the general improvement of oxidation chemistry, research does not only focus on petrochemical-based processes and the improvement of the oxidants, but also involves the incorporation of renewable starting materials.

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

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

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

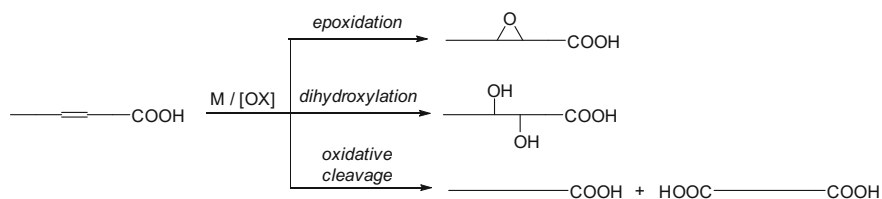


**Fig. 6.1** Overview of important platform chemicals from renewable resources and their industrial applications

## 6.2 Fatty Acids and Fatty Acid Derivatives

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

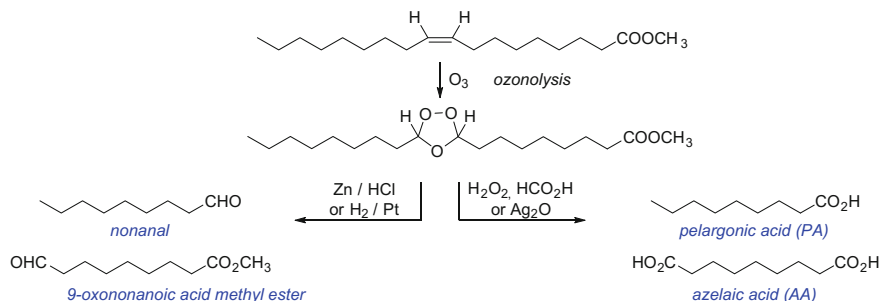
To date, the only commercial source of epoxidised oils is based on the Prileshajev peracid process which lacks of selectivity towards the desired epoxides and harsh reaction conditions, e.g. high concentration of hydrogen peroxide and strong acids [13, 14]. Furthermore, several methods for the epoxidation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



**Fig. 6.2** Selected oxidation reactions of unsaturated fatty acids

on  $\text{H}_2\text{O}_2$ /tungsten heteropolyacids,  $\text{H}_2\text{O}_2$ /methyl trioxorhenium, and enzymatic methods [15–18]. A good epoxidation procedure for the conversion of oleic acid into 9,10-epoxystearic acid in 87% selectivity was developed by Ziólkowski using organic hydroperoxides in the presence of a molybdenum catalyst [19]. Typical homogenous catalyst for the epoxidation of fats and oils with  $\text{H}_2\text{O}_2$  includes  $\text{Mo}(\text{CO})_6$  or  $\text{Mo}(\text{O})_2(\text{acac})_2$  [20]. Epoxy oils and fats can be used as PVC plasticisers, flame retardants, heat stabilisers, additives in lubricants and cosmetics, and many others [21]. Subsequent cleavage of the epoxide structure leads to vicinal diols. A more elegant approach towards diol formation involves the direct dihydroxylation of unsaturated fatty compounds with hydrogen peroxide. For this purpose, tungstic acid ( $\text{H}_2\text{WO}_4$ ) or rhenium complexes such as methyltrioxorhenium ( $\text{CH}_3\text{ReO}_3$ ) are used as catalysts which need to be active under mild reaction conditions (25–50 °C) as shown by Herrmann [22]. Dihydroxylated fatty acids are important materials in chemical, food, and cosmetic industry, as well as crucial signalling compounds related to human disease [23].

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

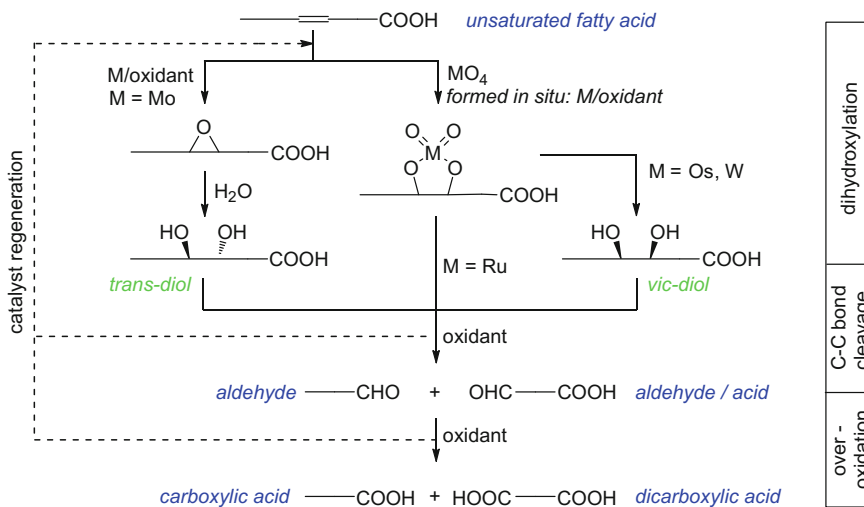


**Fig. 6.3** Traditional preparative double bond cleavage reactions of oleic acid methyl ester via reductive (*left*) and oxidative ozonolysis (*right*) [31]

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

Considering the mechanism of oxidative cleavage of unsaturated fatty acids, it seems more complicated to cleave these functionalised molecules compared to simple or even cyclic alkenes, due to the presence of the carboxylic group causing side reactions and inhibiting radical reaction pathways. Catalytic systems based on transition metal tetroxides can either undergo vic-diol formation in case, e.g. by tungsten ( $\text{H}_2\text{WO}_4/\text{H}_2\text{O}_2$ ) or osmium, while in situ formed  $\text{RuO}_4$  complexes directly cleave the organic tetroxide intermediate (Fig. 6.4). In contrast, the formation of an epoxide followed by hydrolysis to diols was mainly described for, e.g., molybdenum [37].

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



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

field are based on cobalt (Co oleate or naphthenate) [40] or vanadium ( $\text{VO}_4^{3-}/\text{V}_2\text{O}_5$ , 400–500 °C) [41] which lack of reactivity and selectivity towards the desired cleaved products (<45% AA after 72 h). Dapurkar et al. used more active recyclable microporous and mesoporous chromium-, manganese-, and cobalt-coated catalysts in the aerobic double bond cleavage of oleic acid in supercritical  $\text{CO}_2$  which afforded 32% of the C<sub>9</sub>-chain (AA and PA) acids after 8 h [42]. The first breakthrough in oleic acid cleavage regarding high selectivity (yields >90% of AA and PA) was achieved by Kawamoto and Yoshioka in 1982 using  $\text{RuO}_2$  as the catalyst [43, 44]. However, the greatest drawback of this procedure presents the addition of stoichiometric amounts of aldehydes as sacrificial reagents. In continuative research work, Köckritz et al. utilised an osmium catalyst ( $\text{OsO}_4/\text{K}_2\text{OsO}_4$ ) also in combination with an aldehyde as co-oxidant [45]. The formation of the corresponding waste products does not go along with the requirement of green chemistry.

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

According to the limited selectivity of the oxidation of carbon double bonds with  $\text{O}_2$ , different one- and two-step processes were examined for the oxidative cleavage of unsaturated fatty acids with  $\text{H}_2\text{O}_2$ . Apart from oxygen, hydrogen peroxide is the cheapest and also most environmentally friendly oxidant which results in water as the only side product [25]. Industrially,  $\text{H}_2\text{O}_2$  is produced by oxygen reduction in the anthraquinone process developed by BASF [46].

In 1993, first research work regarding the direct oxidative C–C double bond cleavage of oleic acid with  $\text{H}_2\text{O}_2$  was carried out by Katsura who used in situ generated tetrakis-(oxodiperoxo-wolfram)-phosphat in combination with a phase transfer catalyst. In a two-phase system, they reported yields of around 90% of the desired carboxylic acids [47] which led to further optimisation [48–52]. Already one year later, Johnstone et al. published a promising catalyst system based on  $\text{MoO}_3/\text{RuCl}_3/\text{Didecyldimethylammoniumbromid}$  in tert-butanol which yielded 100% AA and 43% PA. After 4 h, the starting material was fully converted, but a large excess of  $\text{H}_2\text{O}_2$  (7–8 equiv.) is required which tends to decompose at the Ru catalysts [53]. A molybdenum-based peroxo complex  $\text{MoO}(\text{O}_2)[\text{C}_5\text{H}_3\text{N}(\text{CO}_2)_2]$  ( $\text{H}_2\text{O}$ ) investigated by Turnwald yielded 82% AA along with equal yields of nonanal after 24 h at 90 °C [52]. Using a heterogeneous tungsten oxide catalyst supported on silica, Nouredini and Kanabur achieved only moderate yields of azelaic acid while the conversion was 86%. Similar yields but lower conversion after 1 h at 130 °C was demonstrated for unsupported tungsten oxid [54]. In 2013, Behr et al. showed that  $\text{Ru}(\text{acac})_3/\text{dipicolinic acid}$  is suitable for the cleavage oleic acid and methyl oleate [55]. In contrast to oleic acid which delivered around 60% of the cleaved C<sub>9</sub>-chain acids, better yields of 81% of azelaic acid methyl ester and 86% of pelargonic acid were obtained after 24 h when using methyl oleate as starting material. Multistep procedures for the production of mono- and dicarboxylic acids include ether epoxidation or dihydroxylation as pointed out in Fig. 6.4. In 1999, Oakley et al. developed a tungsten-based two-step procedure in

which the dihydroxylated intermediates were cleaved by the addition of a cobalt catalyst ( $\text{Co}(\text{acac})_3/\text{N}$ -hydroxyphthalimide) in the presence of oxygen giving a maximum yield of 20% azelaic and perlargonic acid [56]. Since the dihydroxylation of fatty acids was already investigated in much more detail using Re [22, 57], Mo, and W catalysts [34], the studies of Santacesaria et al. due to a deeper understanding of the second reaction step, did dramatically improve the yields of the desired products (56%) [58, 59]. Even better results were obtained with the conditions found by Warwel and Rüscher who used  $\text{Re}_2\text{O}_7/\text{H}_2\text{O}_2$  in the DSME (9,10-dihydroxy-stearic methyl ester)-cleavage achieving yields of 78% [34, 37]. More recently in 2009, Fujitani published the aerobic DSA (9,10-dihydroxy-stearic acid)-cleavage in the presence of Co, Mn, and Co-Mn-Br catalysts which afforded around 90% yields of the desired mono- and dicarboxylic acids [60].

In 2012, the investigation of the catalytic oxidation of methyl oleate showed that the catalyst system  $\text{RuCl}_3/\text{dipicolinic acid}$ , which was already described as a convenient catalyst for the epoxidation of alkenes by Beller and co-workers [61], is also a suitable catalyst for the selective epoxidation of methyl oleate [62]. The epoxide was obtained with high yield amounting to 88%. Further investigations showed that  $\text{RuCl}_3$  as well as the catalyst  $\text{RuCl}_3/\text{dipicolinic acid}$  can also cleave the vicinal diol into the carboxylic acids AA and PA, however, at varied reaction conditions [55]. The systematic optimisation of the reaction led to the formation of azelaic acid monomethyl ester in high yields amounting up to 86%. The catalytic cleavage of the diol with oxygen using a catalyst system of  $\text{Co}(\text{acac})_3$  and  $\text{N}$ -hydroxyphthalimide is also feasible [63]. This reaction was carried out in a small loop-type reactor which enabled very safe oxidation conditions. The carboxylic acids azelaic acid monomethyl ester and perlargonic acid could be synthesized in yields of about 65% each. Recently, vicinal dihydroxy derivatives of oleic acid, methyl oleate, and erucic acid were converted by oxidative cleavage to di- and monocarboxylic acids, respectively, in the presence of highly dispersed gold particles (Au supported on  $\text{Al}_2\text{O}_3$ ) by Köckritz et al. [64]. Although high yields of 86% azelaic acid and 99% perlargonic acid were obtained in 260 min at 80 °C starting from 9,10-dihydroxystearic acid, the main drawback of this system was the significant decrease in the catalytic activity after catalyst recovery.

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

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

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

### 6.3 Terpenes and Terpene Alcohols

Terpenes are hydrocarbons, usually possessing a strong odour, which derive biosynthetically from units of isoprene and are produced by a great variety of plants. Many terpenes autoxidise when they are exposed to air. Among that huge group of secondary metabolites that occur in essential oils and are used as fragrance compounds, there are several examples where the autoxidation is an undesired issue because of allergenic properties of the oxidised products [66]. But on the other hand, directed oxidation of this sufficiently abundant hydrocarbon class, for example in the allylic position, provides functionalised molecules that are important fine chemicals or intermediates [67]. Early work on the oxidation of terpenes using molecular oxygen was already conducted by Reese et al. in 1950 [68]. Ten years later, Bernhard et al. investigated the mechanism of the autoxidation of (+)-limonene [69], which is by far the most industrially relevant monocyclic monoterpene. (+)-Limonene is the major constituent of citrus peel oils and is obtained as a side product from orange juice production. Besides the use as a fragrance, one major limonene-based product is the ketone carvone [70], which can be obtained, e.g., via Wacker-type oxidation (Fig. 6.5). Carvone itself is an excellent starting material for the synthesis of naturally occurring compounds [71, 72]. The monoepoxide limonene oxide, for example accessible using methyltrioxorhenium (MTO) and  $\text{H}_2\text{O}_2$  as the oxidant, represents a precursor for high molecular weight polycarbonate which can be produced by copolymerisation with  $\text{CO}_2$  [73]. The monoepoxide/diepoxide ratio is controllable through the choice of solvent, temperature, and starting material concentrations. Using  $\text{CH}_2\text{Cl}_2$  as the solvent, limonene can be converted completely to the monoepoxides within 30 min at room temperature [18]. Treating limonene under Wacker conditions ( $\text{PdCl}_2/\text{CuCl}_2/\text{LiCl}$ ), the allylic position becomes accessible for the introduction of an oxygen functionality (Fig. 6.5) [74]. The main product of the Wacker oxidation of limonene is carvenyl acetate, which is formed in 87% in the presence of HOAc and  $\text{O}_2$  (1 bar) at 80 °C after 3 h.

Using MTO (methyltrioxo rhenium,  $\text{CH}_3\text{ReO}_3$ ), also bicyclic monoterpenes such as  $\alpha$ -pinene,  $\beta$ -pinene, camphene, and carene can be oxidised.  $\alpha$ -Pinene can be found in concentrations up to 80% in pine oil and is a precursor for several compounds (Fig. 6.6). The epoxide of  $\alpha$ -pinene represents the starting material for the synthesis of campholenic aldehyde [75]. Verbenols, which are used as ingredients in plant protection products and the odour verbenone, are also accessible from  $\alpha$ -pinene. Oxidation of  $\alpha$ -pinene using 0.13 mol% of the complex  $[\text{Co}(\text{4-methylpyridin})_2\text{Br}_2]$ , and  $\text{O}_2$  lead to 76% of verbenone within 7 days [76].



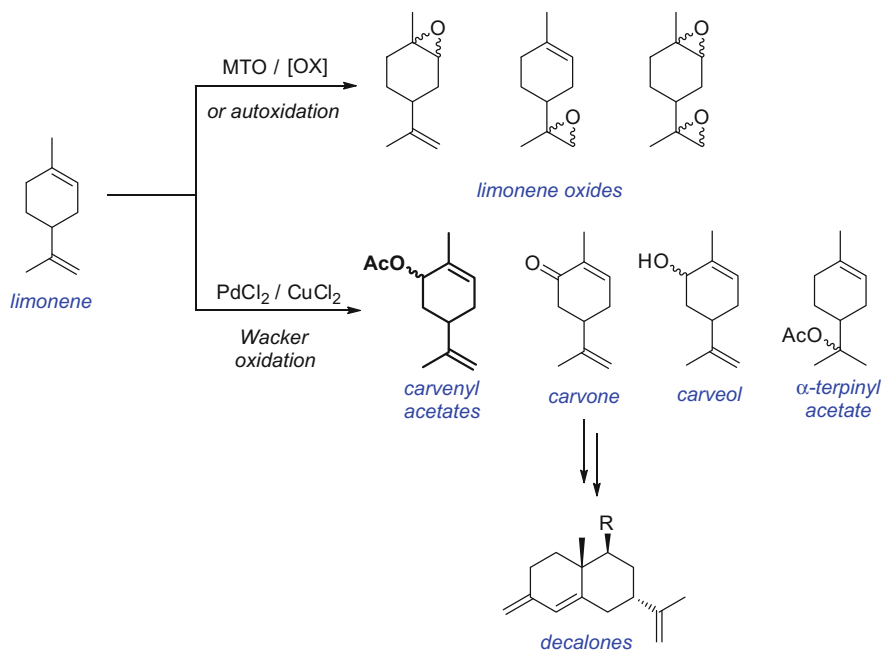


Fig. 6.5 Oxidative modification of limonene

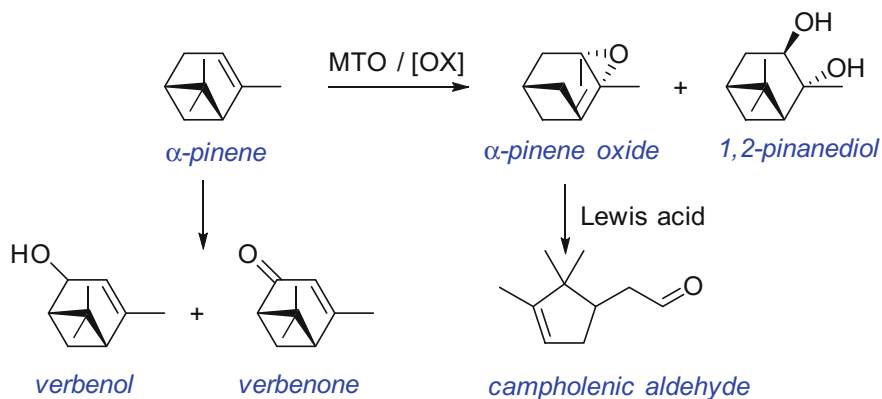
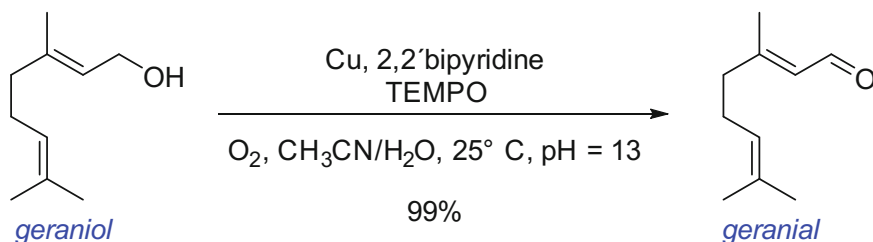


Fig. 6.6 Oxidative modification of  $\alpha$ -pinene [77]

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



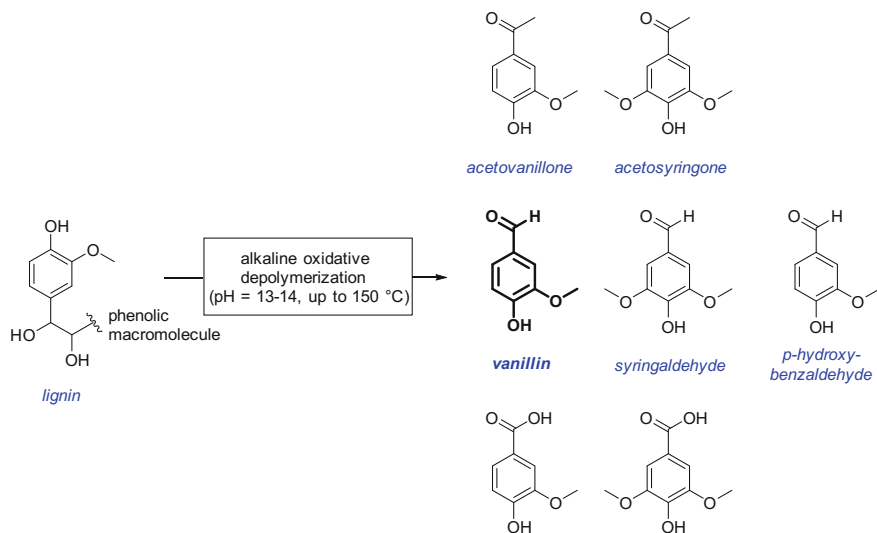
**Fig. 6.7** Environmentally friendly synthesis of the odour geranial

## 6.4 Lignin and Phenylpropanoids

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

Several catalytic methods applied so far to oxidise the renewable source of aromatic compounds. Inorganic catalysts, such as methyltrioxo rhenium (MTO), salen complexes (e.g. Cobalt-Schiff base complexes), vanadium complexes, or polyoxometalates (POMs) (polyoxometallates) achieve an efficient degradation of lignin and lignin model compounds. In relation to other catalysts, MTO represents a quite simple structure that activates molecular oxygen or hydrogen peroxide, whereas with the latter one, also challenging substrates such as activated phenols can be oxidatively upgraded [58, 59]. The excellent reactivity involves overoxidation leading to an increase in functionalisation of the material which might be a useful side effect. An advantage of the salen complex method is its compatibility with aqueous reaction media [81]. Cobalt-Schiff base complexes are able to reversibly react with  $\text{O}_2$  [79]. Modifying the ligands, sterical demand allows to control the oxidation range of lignin. Metal-free organocatalytic systems (for example, TEMPO in combination with NaBr and NaClO), photocatalytic and electrocatalytic oxidations provide a useful alternative to conventional oxidation methods [82]. Biomimetic catalysts also offer appropriate reactivities, for example metal porphyrins [79]. They imitate enzymes (peroxide-dependant ligninase or laccase) which naturally occur in several white-rot fungi [83, 84].

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



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

depolymerisation are shown in Fig. 6.8. While developing a mechanism of the alkaline oxidation reaction starting from the lignin polymer is not a straightforward task [79], the oxidative C–C bond cleavage of the lignin model compound isoeugenol is well described. The isomerisation of the naturally occurring eugenol in the presence of KOH at 250 °C followed by oxidation with  $\text{KMnO}_4/\text{O}_3$  has for a long time been the main industrial process for the production of vanillin, but got nowadays outperformed by the conventional vanillin production based on lignin [87, 88].

## 6.5 Conclusions

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

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