

Review

Pd-mediated epoxidation of olefins

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Abstract

Through the different oxidations of olefins mediated by palladium compounds, the epoxidation has met a limited success. This review summarizes the different stoichiometric and catalytic palladium procedures that led to the production of epoxides from alkenes. The proposed mechanisms are also described with, in some cases, personal comments.

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Keywords: Epoxidation; Olefins; Palladium; Catalysis; Stoichiometric reactions

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1. Introduction

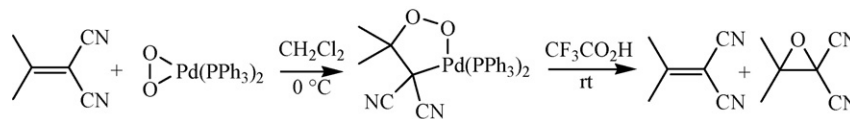
The oxidation of monoolefins in the presence of palladium salts or complexes has led to a plethora of studies. Through the different reactions, the most well known is the Wacker oxidation, a catalytic process that has been intensively used for the synthesis of methyl ketones from terminal olefins [1–4]. Allylic oxidation of olefins is also a common Pd-catalyzed reaction [5] that has been mainly developed for the synthesis of allylic esters [6]. In contrast, the Pd-catalyzed epoxidation of the C=C bonds is so uncommon that in 2000, it was advanced [7] that the corresponding literature contained only two reports, although five studies with Pd catalysis were cited in the 1989 review entitled “Transition-metal-catalyzed epoxidations” [8]. As other studies

were published and new procedures appeared over the recent years, it seems of interest to review this topic.

A range of reports, mainly patents, claims the use of mixtures of palladium and titanium or vanadium compounds for the catalytic epoxidation of light alkenes under a H₂/O₂ atmosphere [9–11]. The role of palladium in these systems is mainly the formation of H₂O₂ from H₂/O₂ mixtures; this is indeed a synthetic method of H₂O₂ [12,13]. The peroxide is then used by the titanium or vanadium compound to perform the epoxidation, a well established catalyzed reaction of these transition metals [14,15]. The presence of palladium can nevertheless modify the efficiency of the epoxidation step as studied with propylene [16] and allyl chloride [17] as substrates. Other bimetallic systems containing palladium have been disclosed [18,19], but these methods, as those above, are out of the scope of this review which is limited to epoxidations mediated by only palladium compounds with, however, an extension to heteropolyoxomet-

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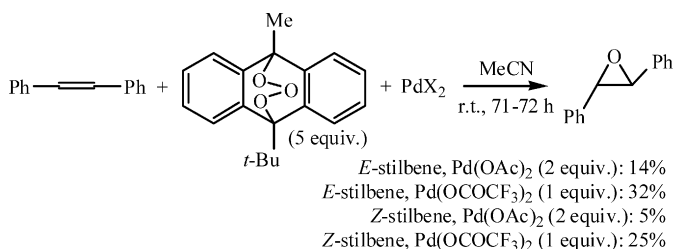
Scheme 1.

alates having a Pd heteroatom. After the presentation of alkene epoxidations involving stoichiometric amounts of palladium complexes, the catalytic procedures will be summarized with, firstly, an arrangement dependent on the nature of the oxygen source and, secondly, a chronological account of the reports.

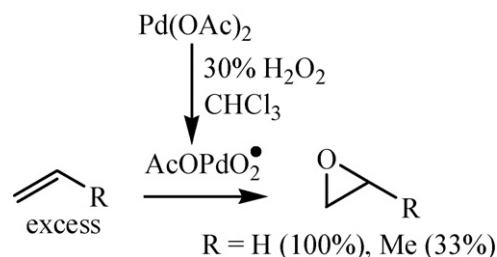
2. Stoichiometric reactions

In 1975, Sheldon and van Doorn reported the cycloaddition of $(\text{Ph}_3\text{P})_2\text{PdO}_2$ to 2-(propan-2-ylidene)malononitrile, and the acidic cleavage of the resulting cyclic peroxy-adduct into a 1:2 mixture of olefin and epoxide (Scheme 1) [20].

Ten years later, Matsuura et al. disclosed the formation of *E*-stilbene oxide via the reaction, in acetonitrile and at room temperature, of *E*- or *Z*-stilbene with a Pd^{II} salt and the ozonide obtained from 9-*t*-butyl-10-methylanthracene (Eq. (1)) [21]. Given the lack of stereospecificity of the process, the decrease of yields in the presence of a radical scavenger, and the similar reaction obtained under thermal conditions [22], the authors proposed a radical mechanism. The Pd^{II} salt would cleave an O–O bond of the ozonide to afford the corresponding peroxy radical intermediate that would react with the C=C bond of the substrate. The scope of this Pd-mediated epoxidation method is very limited since styrene led only to acetophenone under similar conditions.

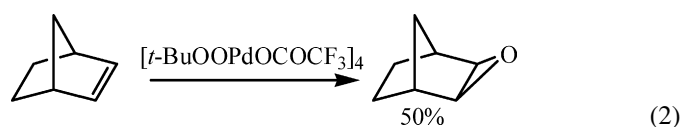


Simultaneously to the above report, Talsi et al. described the oxidation of linear alkenes by a palladium superoxo complex (Scheme 2) obtained from $\text{Pd}(\text{OAc})_2$ and hydrogen peroxide, and identified from its EPR parameters [23]. Subsequently, palladium superoxo complexes possessing similar oxidation properties have been prepared using KO_2 instead of H_2O_2 , and also from $\text{Pd}(\text{OPr})_2$ [24].

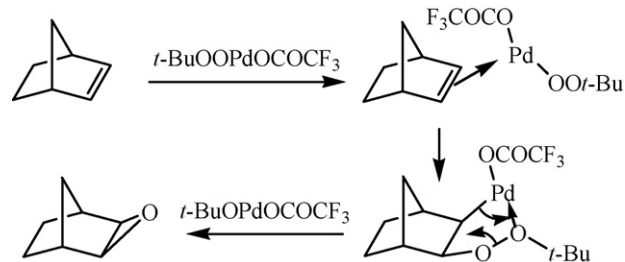


Scheme 2.

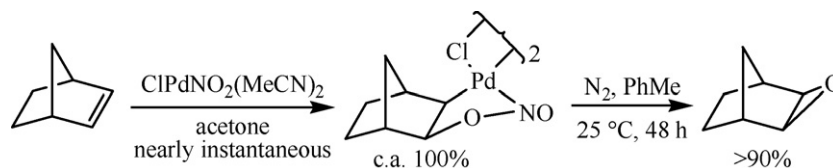
The reactivity of Talsi's palladium superoxo complexes contrasts with that of alkylperoxopalladium complexes which do not epoxidize the linear alkenes [25–27]. In contrast, a cycloalkene such as norbornene underwent oxidation with Mimoun's complex, $(t\text{-BuOOPdOCOCF}_3)_4$ [25], into exo-epoxynorbornene (Eq. (2)) [28]. Given the intermediate proposed by Mimoun for the ketonisation of terminal alkenes with this complex [25,29,30], we suspect the mechanism depicted in Scheme 3. The epoxidation of cycloalkenes with $(t\text{-BuOOPdOCOCF}_3)_4$ seems to be limited to strained substrates since, under similar conditions, cycloheptene afforded cycloheptenol (11%), cycloheptenone (33%) and cycloheptanone (1%) [28].



Andrews and Chen have obtained epoxides from the reaction between cycloalkenes, in particular cycloheptene, and stoichiometric amounts of $\text{ClPdNO}_2(\text{MeCN})_2$ (Eq. (3)) [28,31,32].



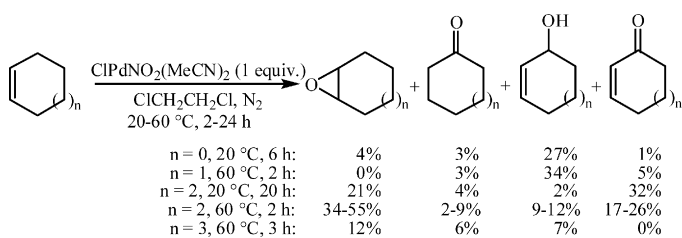
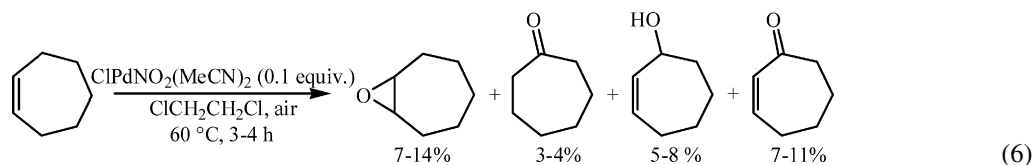
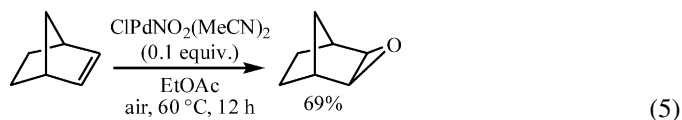
Scheme 3.



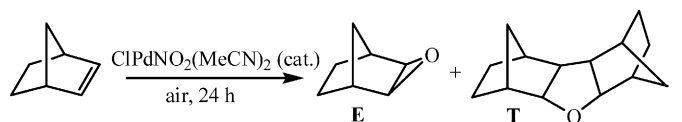
Scheme 4.

With norbornene as the substrate, these authors isolated a heteropalladocyclopentane which, upon standing in toluene, slowly evolved to exo-epoxynorbornene (Scheme 4) [28]. This epoxide has also been efficiently obtained without isolation of the intermediate [31]. Unlike cycloalkenes, the stoichiometric oxidation of linear alkenes with $\text{ClPdNO}_2(\text{MeCN})_2$ afforded, on the best, traces of the corresponding epoxides [31].

the presence of CuCl_2 [35,36] suggests that for oxidations with $\text{ClPdNO}_2(\text{MeCN})_2$, copper salts cannot be used to regenerate active epoxidation species.



Wong et al. have observed that the course of the norbornene reaction mediated by the $\text{ClPdNO}_2(\text{MeCN})_2/\text{air}$ system depended greatly on the substrate concentration, a high concentration leading to a tetrahydrofuran derivative (Eq. (7)). The authors have shown that this compound results from the reaction of the heteropalladocyclopentane depicted in Scheme 4 with the substrate [38].

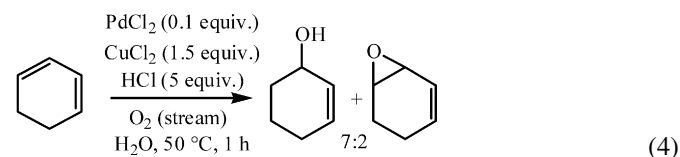


PhMe, [substrate] = 0.04 M, 25 °C: turnover number = 0.55, E/T = 94:6
 PhMe, [substrate] = 1 M, 25 °C: turnover number = 5.3, E/T = 11:89
 PhMe, [substrate] = 2 M, 25 °C: turnover number = 4.9, E/T = 6:94
 PhMe, [substrate] = 4 M, 25 °C: turnover number = 4.4, E/T = 3:97
 EtOAc, [substrate] = 0.04 M, 60 °C: turnover number = 7.3, E/T = 98:2
 EtOAc, [substrate] = 4 M, 60 °C: turnover number = 4.2, E/T = 2:98

3. Catalytic reactions

3.1. Molecular oxygen as oxygen source

In 1978, Paraskewas and Konstantinidis disclosed the formation of a mixture of 2-cyclohexen-1-ol and 2,3-epoxycyclohexene from the PdCl_2 -catalyzed oxidation of 1,3-cyclohexadiene with an oxygenated acidified aqueous solution of CuCl_2 (Eq. (4)). Unfortunately, the yields were not indicated [33].

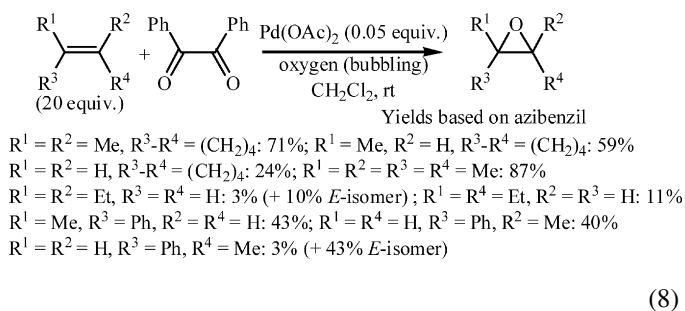


Four years later, Andrews and Cheng reported catalytic conditions for the efficient epoxidation of norbornene using $\text{ClPdNO}_2(\text{MeCN})_2$ under air atmosphere (Eq. (5)) [28,31,34]. The oxidation of cyclopentene and cycloheptene was much less selective (Eq. (6)). Subsequently, Waegell et al have extended the catalytic epoxidation with the $\text{ClPdNO}_2(\text{MeCN})_2/\text{air}$ system to a range of norbornene derivatives using benzene as the solvent (turnover number up to 10) [35,36]. Under similar conditions, terminal olefins such as 1-decene and styrene, led to the corresponding methyl ketones as the main products without formation of epoxides [31,35–37]. The formation of the heteropalladocyclopentane shown in Scheme 4 has been considered as the intermediate leading to exo-epoxynorbornene under catalytic conditions. The study of the reactivity of this complex in

Palladium supported on alumina did not induce the epoxidation of ethylene by oxygen [18], while palladium supported on an inert copper–magnesium–aluminium hydrotalcite catalyzed epoxidation of limonene but with both low conversion and low selectivity [39]. Dyer obtained low amounts of propylene oxide from the passing of a mixture of propylene, and oxygen through a solution of $\text{PdCl}_2[\text{P}(\text{C}_6\text{F}_5)_2]$ in *t*-butanol or 1,2-dichlorobenzene [40]. Cabrera et al. obtained less than 1% of oxidation products with, at best, traces of epoxide from the reaction of cyclohexene using oxygen and catalytic amounts of $\text{Pd}(\text{acac})_2$ in refluxing benzene or toluene [41]. In contrast, epoxidation of cyclohexene was the main reaction pathway occurring with oxygen generated on the palladium anode during electrolysis of water [42].

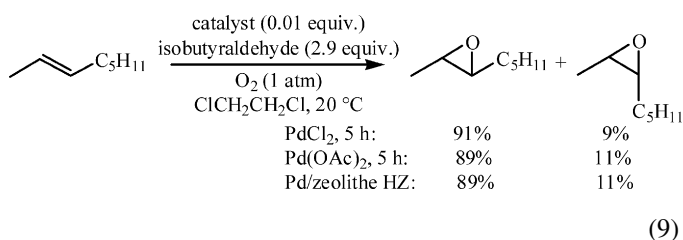
A few papers report Pd-catalyzed epoxidations using an agent which in situ interacts with molecular oxygen. To our knowledge, the first report concerns the association $\text{O}_2/\text{azibenzil}$ that, in the presence of catalytic amounts of $\text{Pd}(\text{OAc})_2$, led to the epoxidation of various olefins (Eq. (8)) [43]. According to Ryang and Foote, a carbene–palladium complex obtained from the Pd-catalyzed decomposition of azibenzil reacts with oxygen to afford the epoxidation species. The oxygen-transfer to the olefin remains undetermined but the lack of stereospecificity indicates a stepwise mechanism with an intermediate which can rotate. Although this method has allowed the epoxidation of various

types of olefins, the large excess of the substrate compared to the amount of azibenzil limits its usefulness.



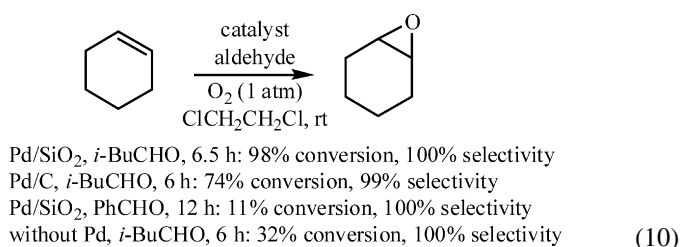
(8)

With isobutyraldehyde as the additive, Bregeault et al. have epoxidized *E*-2-octene in high yields using various Pd-catalysts at both ambient temperature and oxygen pressure (Eq. (9)) [44]. The authors suggest the in situ generation of isobutyric peracid which would afford an oxopalladium complex. Both peracid and oxo complex would mediate the epoxidation step. Interestingly, the supported catalyst, namely Pd/zeolithe HZ, has been recycled without loss of its activity. Under similar experimental conditions, the Pd(acac)₂-catalyzed reaction of α -pinene with isobutyraldehyde/O₂ did not afford the corresponding epoxide [45].

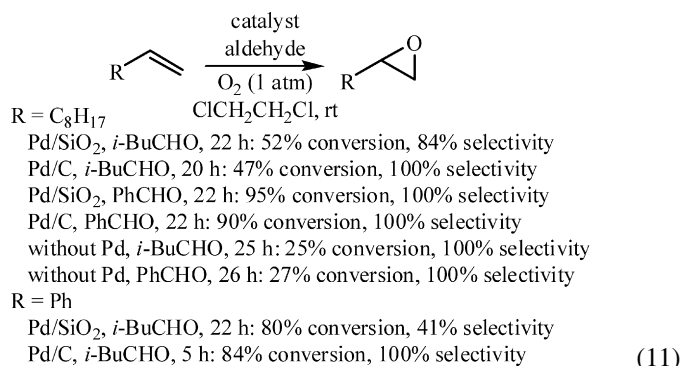


(9)

Seven years later, Gao and Angelici who, apparently, were not aware of above Bregeault's study, have reported the oxidation of various olefins using supported Pd catalysts and the isobutyraldehyde or benzaldehyde/O₂ association. Conversion and selectivity were quite depending on the substrate, aldehyde and support (Eqs. (10) and (11)) [46]. These authors have observed epoxidation even in the absence of the metal but with much lower efficiency (Eqs. (10) and (11)), and have identified isobutyric acid as by-product of isobutyraldehyde. The formation of this acid, as the metal-free epoxidation, agrees with the in situ formation of peracids.



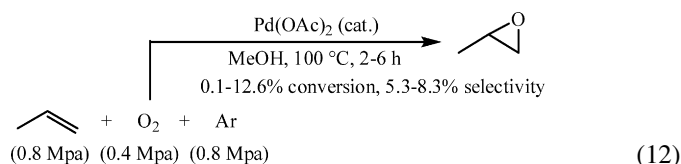
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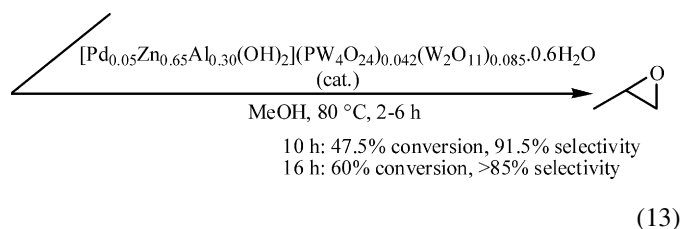
(11)

A Japanese patent discloses the use of an aliphatic or aromatic nitrile as additive for the epoxidation with oxygen of propylene and butenes catalyzed by Pd black or PdCl₂: low conversions and selectivities were obtained [47]. We suspect that autooxidation of the nitrile [48] is involved in this epoxidation process.

Liu et al. have intensively studied the catalytic oxidation of propylene at 100 °C in MeOH. Pd(OAc)₂ as catalyst led to low amounts of propylene oxide (Eq. (12)) [49–51]. While 1,10-phenanthroline as ligand increased the conversion but suppressed the formation of the epoxide [49], the addition of peroxy-heteropoly compounds, in particular [(C₆H₁₃)₄N₃{PO₄[W(O)(O₂)₂]₂]₄}, led to high selectivities towards propylene oxide and good conversions [50,51]. These observations led the authors to prepare efficient recyclable supported catalysts [52,53]. Given the marked activity decrease of these catalytic systems when MeCN was used as solvent instead of MeOH [49,51], the formation of HOCH₂OOH or H₂O₂ from Pd-catalyzed reaction between MeOH and oxygen has been proposed [51,53,54]. When a peroxy-heteropoly compound is used as additive, this one will be the real epoxidation species, its regeneration being assumed with the peroxide synthesized via the Pd catalyst [51,53]. Recently, Liu's team has prepared a new peroxy-polyoxometallate that is an effective reusable epoxidation catalyst of propylene (Eq. (13)), and has demonstrated the determining role of the palladium on the reactivity [55].



(12)

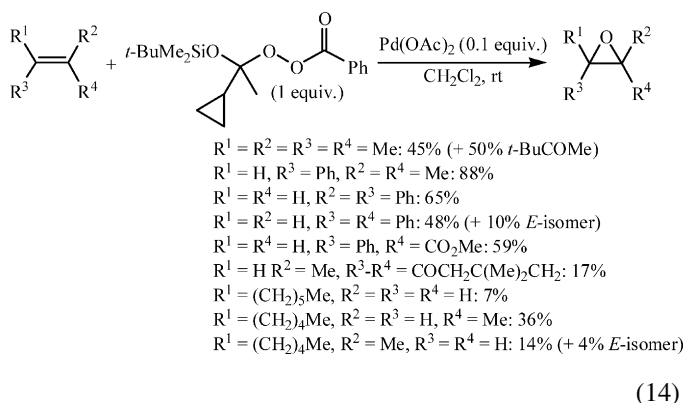


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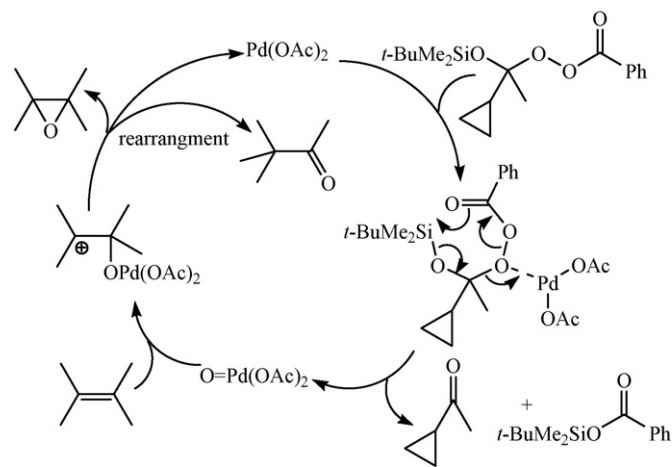
3.2. Peroxides as oxygen sources

To our knowledge, the first Pd-catalyzed epoxidation of olefins by a peroxide has been discovered by Saito et al. using

α -silyloxyalkyl peroxybenzoates (Eq. (14)) [56]. Given the lack of stereospecificity, the authors suggested a stepwise mechanism with an intermediate which can rotate. Based on ^{18}O -labelling studies and the structures of rearranged products, epoxidation mediated by a Pd^{IV} -oxo species as outlined in Scheme 5 was proposed. Although the reaction pathway leading to $(\text{AcO})_2\text{Pd}^{\text{IV}}\text{O}$ is not obvious, this proposal agrees with the formation of pinacolone from 2,3-dimethyl-2-butene (Eq. (14)), as well as 1-cyclopropylethanone and *t*-butyldimethylsilyl benzoate which have also been isolated in high yields (95 and 76%, respectively) as side products from the oxidation of *E*-stilbene. The alternative oxidative species suggested in the original report [56] is the Pd^{II} -peroxybenzoate, AcOPdOOCOPh , which presents similarities with $(\text{Ph}_3\text{P})_2\text{ClPtOOCOPh}$, an epoxidation complex of olefins [57]. Subsequently, Nagata and Saito have envisaged the formation of $(\text{AcO})(\text{PhCO}_2)\text{Pd}^{\text{IV}}\text{O}$ from AcOPdOOCOPh (Scheme 6) and the reaction of the oxopalladium complexes with $\text{Pd}(\text{OAc})_2$ (Scheme 7) [58]. Note however that, the same team has used $\text{Cu}(\text{OCOCF}_3)_2$ as the catalyst, with improved results from terminal or single internal olefins, and, as previously, the formation of 1-cyclopropylethanone and *t*-butyldimethylsilyl benzoate [59].

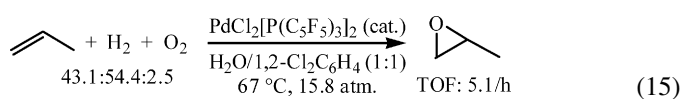


In the above section, the in situ production of hydrogen peroxide was suspected under Liu's conditions. In 1980, Rousel and Mimoun reported that terminal olefins were oxidized into the corresponding methyl ketones using H_2O_2 and various Pd^{II} catalysts at 80°C in AcOH or *t*-BuOH, while internal and cycloolefins such as cyclohexene were unreactive [60]. Nevertheless, the use of the in situ produced H_2O_2 was reported by Dyer in a German patent for the Pd-catalyzed epoxidation of propylene: the epoxide was isolated from the passing of a mixture of propylene, hydrogen and oxygen in an aqueous

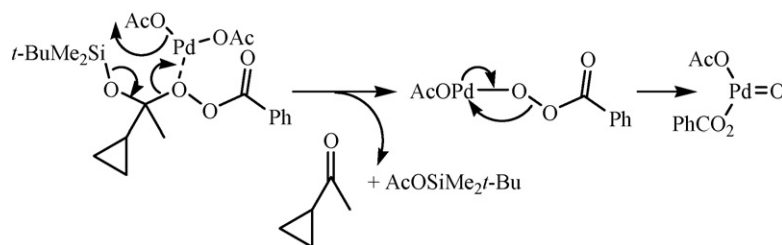


Scheme 5.

solution of a Pd^{II} catalyst (Eq. (15)) [40]. This author noted the strong decrease of the process efficiency in the absence of hydrogen, and, subsequently, he patented the synthesis of H_2O_2 under similar conditions, except the presence of the olefin [12].

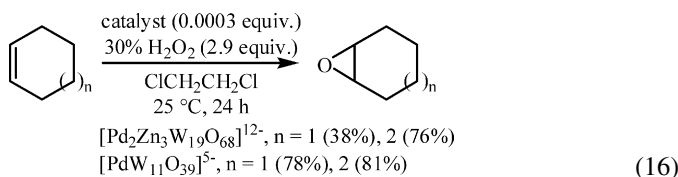


The use of commercial H_2O_2 for Pd-catalyzed epoxidations has been subsequently reported. Neumann and Khenkin used a polyoxometallate substituted with Pd^{II} , $\text{K}_{12}\{[\text{WZnPd}_2(\text{H}_2\text{O})_2](\text{ZnW}_9\text{O}_{34})_2\}$ [61,62] Methathetical exchange by addition of methyltricaprylammonium chloride has led to a catalyst effective for the epoxidation of cyclooctene while, for cyclohexene, allylic oxidation was a competing reaction (Eq. (16)). Catalysis with a monosubstituted Keggin compound improved the results, particularly those from cyclohexene (Eq. (16)). Under similar conditions, 1-octene afforded a low yield (4.5–5.6%) of the corresponding epoxide while catalysis by $(\text{R}_4\text{N})_2\text{PdCl}_4$ led only to 2-octanone. The oxide products are typical of tungsten–hydrogen peroxide oxidations [63], but kinetic studies and comparison of reactivities with a non-noble metal substituted compound, $\{(\text{WZn}_3)(\text{ZnW}_9\text{O}_{34})_2\}^{12-}$, have indicated a special effect of a neighboring palladium atom to a tungsten center for the disubstituted $\{[\text{WZnPd}_2(\text{H}_2\text{O})_2](\text{ZnW}_9\text{O}_{34})_2\}^{12-}$

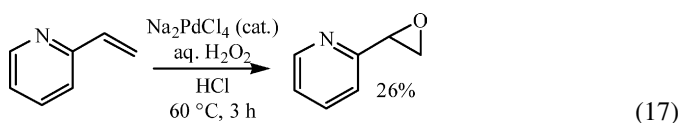


Scheme 6.

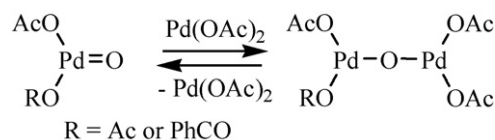
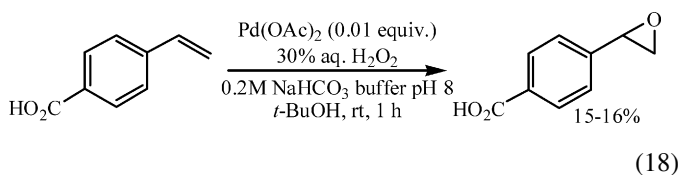
catalyst [61].



A Japanese patent claimed the epoxidation of vinylpyridines in 26% yield with H_2O_2 and catalytic amounts of Na_2PdCl_4 in the presence of hydrochloric acid (Eq. (17)) [64]. In contrast, no more than 5% of styrene oxide was obtained from styrene using H_2O_2 and various chelated Pd^0 and Pd^{II} complexes [65], while with PdCl_2 , the formation of this epoxide was not mentioned [66].

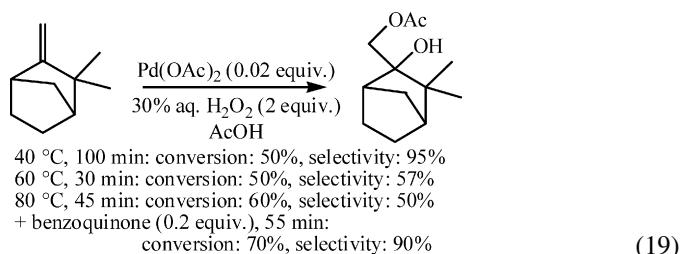


With 30% aqueous H_2O_2 as the oxygen source, Jacobsen and Francis have only detected minute amounts of epoxide from the oxidation, catalyzed by $\text{Pd}(\text{OAc})_2$ coordinated to supported imine ligands, of *E*- β -methylstyrene in a $\text{CH}_2\text{Cl}_2/t$ -BuOH mixture [67], while Burgess et al. obtained 15–16% of epoxide from the $\text{Pd}(\text{OAc})_2$ -catalyzed oxidation of 4-vinylbenzoic acid (Eq. (18)) [68]. The epoxide was a minor constituent (no more than 12% yield) of the reaction, catalyzed by various Pd^{II} salts (PdCl_2 , PdBr_2 , $\text{Pd}(\text{OAc})_2$, $\text{Pd}(\text{acac})_2$), of α -pinene with H_2O_2 or $\text{H}_2\text{O}_2/\text{O}_2$ at 70 °C in MeCN [69].

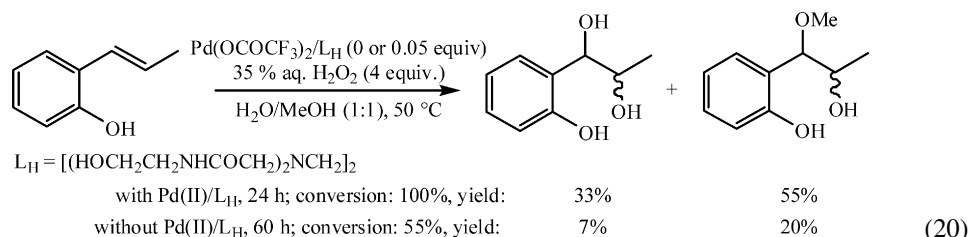


Scheme 7.

and the two possible routes depicted in Scheme 8, one of them involving the transient epoxidation of the C=C bond, have been suggested.



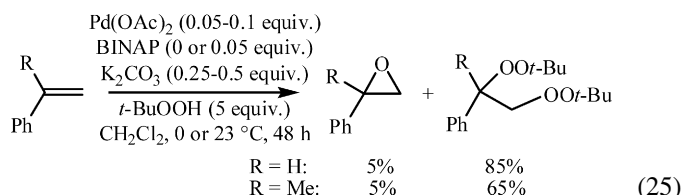
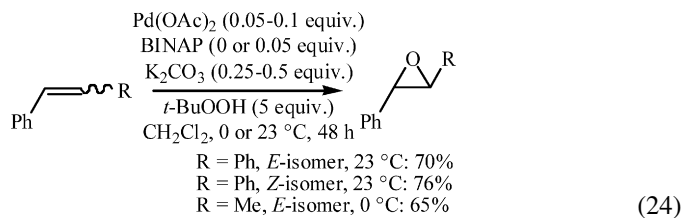
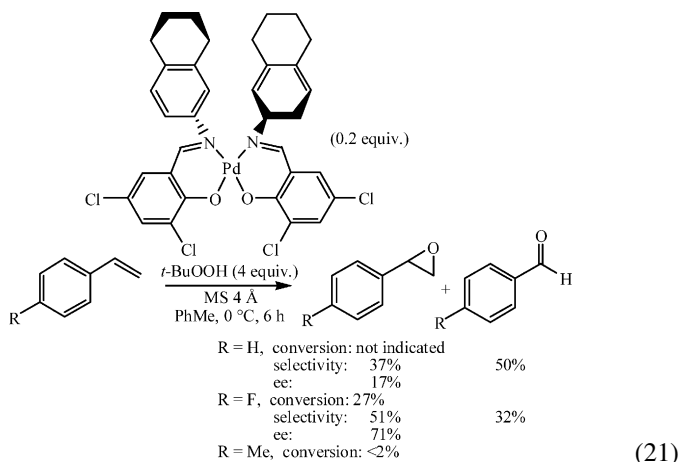
In 2005, we disclosed that the oxidation of 2-(*E*-prop-1-enyl)phenol with H_2O_2 in water/methanol, catalyzed by $\text{Pd}(\text{OCOCF}_3)_2$ associated to the hydrosoluble ligand $[(\text{HOCH}_2\text{CH}_2\text{NHCOCF}_3)_2\text{NCH}_2]_2$, afforded a mixture of 2-(1,2-dihydroxypropyl)phenol and 2-(2-hydroxy-1-methoxypropyl)phenol (Eq. (20)). The reaction occurred also in the absence of palladium but was less effective (Eq. (20)) [71]. Mechanistic experiments and ESI-MS studies have supported the formation of 2-(3-methyloxiran-2-yl)phenol as intermediate (Scheme 9) [72]. The phenol-mediated epoxidation of alkenes by H_2O_2 disclosed by Jacobs et al. [73] rationalize the epoxidation without metal, while the known instability of 2-(3-methyloxiran-2-yl)phenol [74] explains our inability to isolate this particular epoxide.



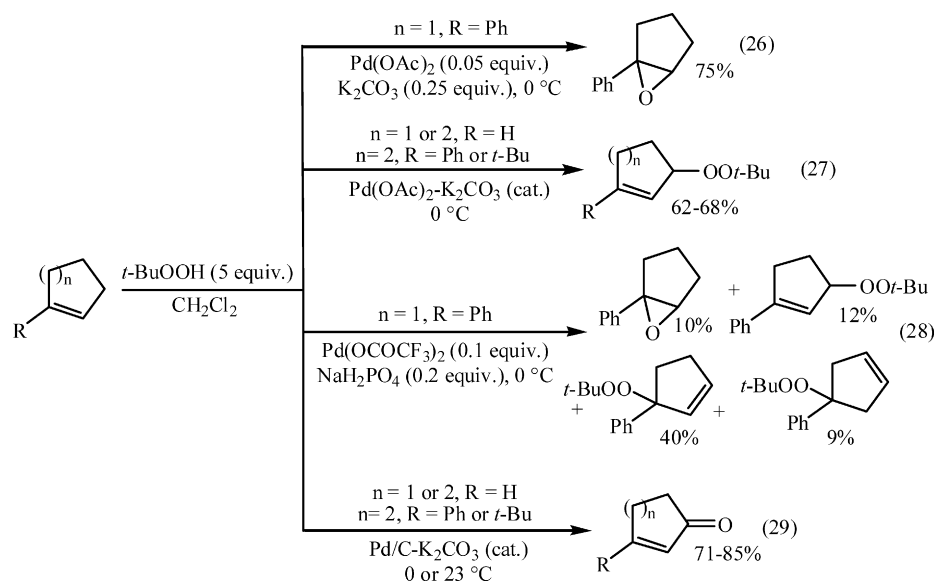
Under experimental conditions similar to those of Mimoun [60] but with a particular substrate, namely camphene, Gusevskaya et al. obtained (2-hydroxy-3,3-dimethylbicyclo[2.2.1]heptan-2-yl)methyl acetate with a selectivity increased in the presence of benzoquinone (Eq. (19)) [70]. According to the authors, the reaction was not due to the possible in situ generation of peroxyacetic acid since this glycol monoacetate was not formed in the absence of the palladium acetate. A reaction mediated by hydroperoxypalladium species,

Che et al. investigated the enantioselective epoxidation of styrenes with *t*-BuOOH and chiral binaphthyl Schiff base complexes of palladium. Efficiencies, selectivities and enantioselectivities depended markedly on the substitution of the aryl group (Eq. (21)). The epoxidation of β -methylstyrenes resulted in no more than 5% enantioselectivity and was non-stereospecific from the *Z*-isomer. According to ESI-MS analysis, a palladium complex bearing the chiral ligand and either *t*-BuOOH or *t*-BuOO moiety would be in situ

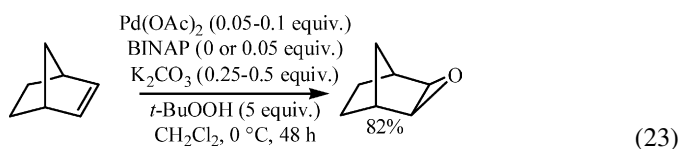
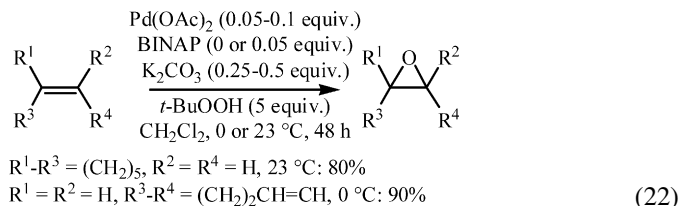
formed [7].



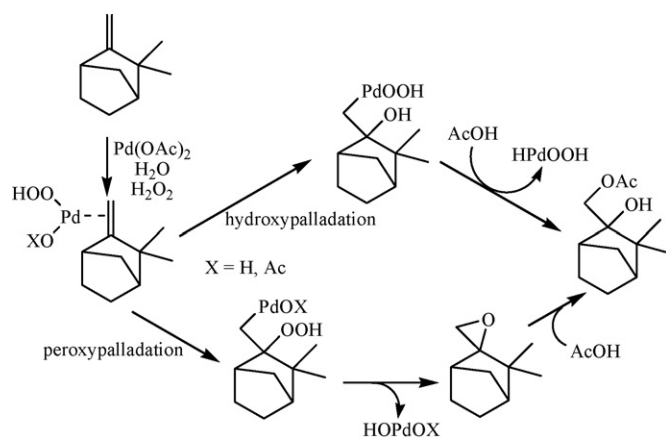
Subsequently, Corey and Yu obtained high yields of epoxides from a range of olefins using *t*-BuOOH and catalytic amounts of Pd(OAc)₂, K₂CO₃ and, in some cases, BINAP (Eqs. (22)–(25)). The course of the reaction was very sensitive to the nature of the



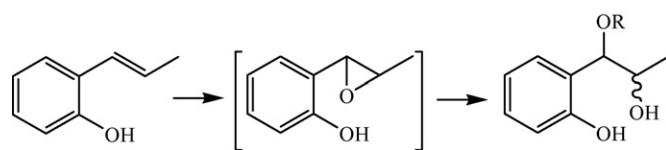
substrate, base and ligands as shown in Eqs. (26)–(29); allylic *t*-butylperoxidation or allylic ketonisation can be the main reactive pathways (Eqs. (25), (27)–(29)) [75].



According to mass spectral and ¹H NMR analyses, the addition of *t*-BuOOH to the Pd(OAc)₂/K₂CO₃ mixture leads to the exchange of both carboxylate ligands to afford Pd(OO*t*-Bu)₂ species [75]. Given the absence of stereospecificity of the oxidation of *Z*-stilbene (Eq. (24)), Corey and Yu excluded an epoxidation occurring via the insertion of the C=C bond into a Pd-OO*t*-Bu bond; they proposed the free radical chain process shown in Scheme 10 which involves a two step epoxidation mediated by the addition of *t*-BuOO•, initially issued from the decomposition of Pd(OO*t*-Bu)₂ species, to the C=C bond. This proposal is in agreement with the reaction pathways of *Z*-stilbene [76] (lack of the epoxidation stereospecificity), styrene [77] and α-methylstyrene [78] (formation of a mixture of epoxide and *t*-butylperoxy adducts) induced by *t*-butylperoxyl radicals but seems to disagree with the observed high conversions. We suspect a more complicated mechanism with more

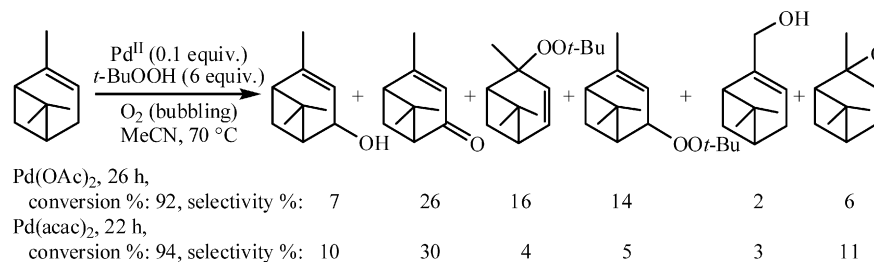


Scheme 8.



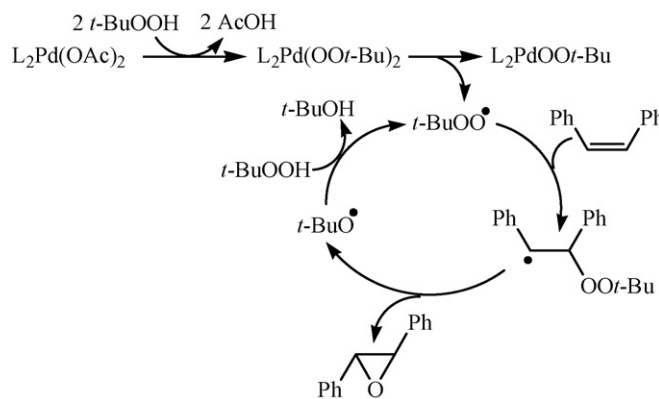
Scheme 9.

involvement of the role of palladium [79]. The low conversion of styrene induced by *t*-BuOOH at 25 °C in CH₂Cl₂ in the absence of catalyst (10% after 48 h) [80], and the low rates of the decomposition of *t*-BuOOH in olefins with the low to moderate epoxidation yields under metal-free condi-



(30)

tions [14,81,82] also indicate that Scheme 10 is oversimplified, and that participation of palladium should be included in the mechanistic cycle. The base and the ligands have also a role. Indeed, the Pd(OCOCF₃)₂-catalyzed oxidation of 1-phenylcyclopentene (Eq. (28)) with a decreased amount of NaH₂PO₄ (0.025 equiv. instead of 0.2 equiv.) suppressed the formation of the epoxide and led only to *t*-butylperoxy ethers [75]. Furthermore, the exchange of Pd(OCOCF₃)₂/NaH₂PO₄ (0.1 and 0.2 equiv., respectively) to Pd(OAc)₂/K₂CO₃ (0.05 and 0.25 equiv., respectively) increased the epoxide yield from 10% (Eq. (28)) to 75% (Eq. (26)). Corey's observation of Pd(OO*t*-Bu)₂ species from *t*-BuOOH and Pd(OAc)₂, differs strongly from those of Mimoun et al. who, under either neutral or acidic conditions, only obtained exchange of one ligand from various Pd(OCOR)₂ (R = Me, CCl₃, C₅H₁₁, CF₃) and have fully characterized the complex (Cl₃CCO₂PdOO*t*-Bu)₄ [25]. Nevertheless, when Corey's reactions were carried out with Pd(OCOCF₃)₂/NaH₂PO₄ instead of Pd(OAc)₂/K₂CO₃, ¹H NMR studies revealed the formation of CF₃CO₂PdOO*t*-



Scheme 10.

Bu species [75]. Consequently, it appears that the pH of the reactive medium has a determining role on the structure of the complexes formed from *t*-BuOOH and Pd(OCOR)₂. Note that the formation of *t*-butylperoxy ethers obtained from 1-phenylcyclopentene using the Pd(OCOCF₃)₂/NaH₂PO₄ system has been explained by peroxypalladation of the olefinic linkage [83] followed by HPdOCOCF₃ elimination [75], a mechanism we have previously assumed for the Pd(OCOCF₃)₂-catalyzed *t*-butylperoxidation of 1-(*p*-toluenesulfonyl)-2-propene by *t*-BuOOH [84].

More recently, Karim et al. reported the Pd^{II}-catalyzed reaction of α -pinene with *t*-BuOOH/O₂ at 70 °C in MeCN: epoxidation was a minor reactive pathway (Eq. (30)) [69].

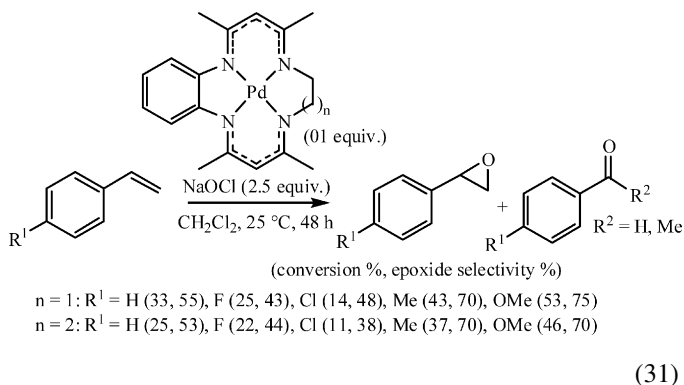
Before to close this section, it is important to point out the relative instability of peroxides in the presence of palladium. Their decomposition providing oxygen, substrates prone to radical allylic peroxidation such as cyclohexene, can afford allylic hydroperoxides. Moreover, palladium could participate in the formation of both allylic radicals [39] and allylic hydroperoxides [85]. Like *t*-BuOOH and HOOH, these hydroperoxides can epoxide the substrate, reaction that could occur even under metal-free conditions, nevertheless with a low efficiency [14,81,86,87]. Of course, the above reaction pathways possibly apply also to epoxidations summarized in Section 3.1, particularly those in low yields.

3.3. Other oxygen sources

With Che's chiral catalysts (Eq. (21)), unreactivity was observed with 2,6-dichloropyridine *N*-oxide as the stoichiometric oxidant while the use of PhIO led to degradation of the catalyst and very low yields of epoxides from styrenes [7]. A

Pd cluster was also inefficient for the epoxidation of styrene with PhIO [88].

Recently, Park et al. have used Pd^{II} complexes having tetraaza-cycloannulenes as ligands to catalyze the oxidation of styrenes with sodium hypochlorite, given mostly the corresponding epoxides. Nevertheless, the efficiency and the selectivity of the process depended on both the size of the ligand and the electronic properties of the aryl substituent (Eq. (31)) [89].



4. Concluding remarks

Actually, there is no general method for the epoxidation of olefins under palladium catalysis, most of them lead to low yields and/or are restricted to particular substrates. Even the method disclosed by Corey and Yu, which, at the present time, seems to be the most powerful, has a limited success: only seven out of sixteen studied substrates have been epoxidized in fair to high yields. The epoxidation efficiency depends not only on the substrate but also on the ligands. These latter can modify the electrophilicity of the metal and, consequently, its reactivity. Thus, the course of the oxidation will depend on the electronic properties of both olefin and palladium compound. Moreover, the mechanism of most epoxidations carried out in the presence of catalytic amounts of palladium remains undetermined [90]; even the role of the metal is uncertain since, in some cases, some epoxidation occurs under palladium-free experimental conditions.

References

- [1] (a) J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, R. Sieber, R. Rüttinger, H. Kojer, *Angew. Chem.* 71 (1959) 176–182;
 (b) J.E. Bäckvall, B. Åkermark, S.O. Ljunggren, *J. Am. Chem. Soc.* 101 (1979) 2411–2416.
- [2] (a) P.M. Maitlis, *The Organic Chemistry of Palladium, Volume II, Catalytic Reactions*, Academic Press, 1971, pp. 82–93;
 (b) R. Jira, W. Freiesleben, in: E.I. Becker, M. Tsutsui (Eds.), *Organometallic Reactions*, vol. 3, Wiley, New York, 1972, pp. 1–190;
 (c) P.M. Henry, *Palladium Catalysed Oxidation of Hydrocarbons*, D. Reidel, Dordrecht, 1980, pp. 41–84.
- [3] (a) J. Tsuji, *Synthesis* (1984) 369–384;
 (b) J.M. Takacs, X.-T. Jiang, *Curr. Org. Chem.* 7 (2003) 369–396;
 (c) G.V.M. Sharma, P.R. Krishna, *Curr. Org. Chem.* 8 (2004) 1187–1209.
- [4] For a review on the Pd-catalyzed synthesis of aldehydes from terminal olefins, see: J. Muzart, *Tetrahedron* 63 (2007) 7505–7421.
- [5] (a) J. Muzart, *Bull. Soc. Chim. Fr.* (1986) 65–77;
 (b) I.I. Moiseev, M.N. Vargaftik, *Coord. Chem. Rev.* 248 (2004) 2381–2391.
- [6] (a) S. Hansson, A. Heumann, T. Rein, B. Åkermark, *J. Org. Chem.* 55 (1990) 975–984;
 (b) B. Åkermark, E.M. Larsson, J.D. Oslob, *J. Org. Chem.* 59 (1994) 5729–5733;
 (c) C. Jia, P. Müller, H. Mimoun, *J. Mol. Catal. A: Chem.* 101 (1995) 127–136;
 (d) K.J. Fraunhoffer, D.A. Bachovchin, M.C. White, *Org. Lett.* 7 (2005) 223–226.
- [7] X.-G. Zhou, J.-S. Huang, X.-Q. Yu, Z.-Y. Zhou, C.M. Che, *J. Chem. Soc., Dalton Trans.* (2000) 1075–1080.
- [8] K.A. Jørgensen, *Chem. Rev.* 89 (1989) 431–458.
- [9] (a) R. Meiers, U. Dingerdissen, W.F. Hölderich, *J. Catal.* 176 (1998) 376–386;
 (b) T. Hayashi, K. Tanaka, M. Haruta, *J. Catal.* 178 (1998) 566–575;
 (c) R. Meiers, W.F. Hölderich, *Catal. Lett.* 59 (1999) 161–163;
 (d) W. Laufer, W.F. Hölderich, *Appl. Catal. A: Gen.* 213 (2001) 163–171;
 (e) G. Jenzer, T. Mallat, M. Maciejewski, F. Eigenmann, A. Baiker, *Appl. Catal. A: Gen.* 208 (2001) 125–133;
 (f) T. Danciu, E.J. Beckman, D. Hancu, R.N. Cochran, R. Grey, D.M. Hajnik, J. Jewson, *Angew. Chem. Int. Ed.* 42 (2003) 1140–1142;
 (g) E.J. Beckman, *Green Chem.* 5 (2003) 332–336.
- [10] (a) A. Sato, T. Miyake, *Jpn. Kokai Tokkyo Koho JP 04352771* (1992); *Chem. Abstr.* 118, 169776.;
 (b) R.N. Cochran, J.C. Jubin Jr., M.A. Liepa, R. Nedwick, R. Pitchai, W.W. Wentzheimer, US 5,973,171 (1999); *Chem. Abstr.* 131, 286940.;
 (c) R.M. Dessau, A.P. Kahn, R.A. Grey, C.A. Jones, J.D. Jewson, *PCT Int. Appl. WO 9952885* (1999); *Chem. Abstr.* 131, 300778.;
 (d) R.M. Dessau, A.P. Kahn, R.A. Grey, *PCT Int. Appl. WO 9952884* (1999); *Chem. Abstr.* 131, 300777.;
 (e) R.A. Grey, U.S. Patent US 6,063,942 (2000); *Chem. Abstr.* 132, 336090.;
 (f) R.A. Grey, U.S. Patent US 6,403,815 (2002); *Chem. Abstr.* 137, 7794.;
 (g) R.A. Grey, U.S. Patent US 6,441,204 (2002); *Chem. Abstr.* 137, 185989.;
 (h) R.A. Grey, C.A. Jones, U.S. Patent US 6,498,259 (2002); *Chem. Abstr.* 138, 39702.;
 (i) J.C. Jubin Jr., R.A. Grey, U.S. Patent US 6,867,312 (2005); *Chem. Abstr.* 142, 298451.;
 (j) R.A. Grey, E. Morales, U.S. Patent US 171,365 (2005); *Chem. Abstr.* 143, 172746.;
 (k) R.A. Grey, M.P. Kaminsky, U.S. Patent US 187,095 (2005); *Chem. Abstr.* 143, 230359.;
 (l) M.P. Kaminsky, U.S. Patent US 7,026,492 (2006) *Chem. Abstr.* 144, 351173.;
 (m) M.P. Kaminsky, R.A. Grey, U.S. Patent US 277,542 (2005); *Chem. Abstr.* 144, 52057.;
 (n) K. Qin, R.A. Grey, P.J. Whitman, U.S. Patent US 7,057,056 (2006); *Chem. Abstr.* 145, 27836.;
 (o) Y. Masaki, *Jpn. Kokai Tokkyo Koho JP 10017559* (1998); *Chem. Abstr.* 128, 127921.;
 (p) U. Müller, P. Lingelbach, P. Basler, W. Harder, K. Eller, V. Kohl, J. Dembowski, N. Reiber, M. Fischer, *Ger. Offen. DE 4425672* (1996); *Chem. Abstr.* 124, 205575.;
 (q) U. Müller, G.H. Grosch, M. Schulz, N. Rieber, *Ger. Offen. DE 19600709* (1997); *Chem. Abstr.* 127, 150397.;
 (r) G.H. Grosch, U. Müller, M. Schulz, N. Rieber, H. Wurz, *PCT Int. Appl. WO 9747386* (1997); *Chem. Abstr.* 128, 61904.;
 (s) J.D. Jewson, C.A. Jones, R.M. Dessau, *PCT Int. Appl. WO 062380* (2001); *Chem. Abstr.* 135, 195939.;
 (t) B. Cooker, J.D. Jewson, W.H. Onimus, U.S. Patent US 6,281,369 (2001); *Chem. Abstr.* 135, 195935.
- [11] (a) D. Hancu, U.S. Patent US 6,399,794 (2002); *Chem. Abstr.* 137, 6577.;
 (b) D. Hancu, E.J. Beckman, T. Danciu, U.S. Patent US 073,856 (2003); *Chem. Abstr.* 138, 304685.;
 (c) J. Seeba, A.-J. Nagy, S. Voelkening, G. Wiessmeier, *Eur. Pat. Appl. EP 1281705* (2003); *Chem. Abstr.* 138, 137728.;
 (d) B. Zhou, M. Rueter, U.S. Patent US 6,534,661 (2003); *Chem. Abstr.* 138, 239699.;

- (e) R.N. Cochran, P.G. Balan, M.A. Liepa, B. Cooker, U.S. Patent US 6,710,194 (2004); Chem. Abstr. 140, 271376.;
- (f) S. Feng, Y. Wang, J. Bi, X. Wang, G. Yu, C. Wu, X. Liu, D. Zhao, W. Fu, Faming Zhuanyi Shenqing Gongkai Shuomingshu CN 1387948 (2003); Chem. Abstr. 141, 7623.;
- (g) J.F. Miller, US 6,884,898 (2005); Chem. Abstr. 142, 411821.;
- (h) P.J. Whitman, J.F. Miller, J.H. Speidel Jr., R.N. Cochran, U.S. Patent US 7,138,535 (2006); Chem. Abstr. 145, 489107.;
- (i) R.M. Dessau, U.S. Patent US 187,394 (2005); Chem. Abstr. 143, 230361.;
- (j) W.H. Onimus, B. Cooker, U.S. Patent US 6,972,337 (2005) Chem. Abstr. 144, 23241.;
- (k) C. Corma, D. Avelino, E. Marcelo, PCT Int. Appl. WO 111600 (2006); Chem. Abstr. 145, 471365.
- [12] (a) P.N. Dyer, F. Moseley, Eur. Pat. Appl. EP 38700 (1981); Chem. Abstr. 96, 106643.;
- (b) P.N. Dyer, F. Moseley, Eur. Pat. Appl. EP 38701 (1981); Chem. Abstr. 96, 71283.
- [13] (a) P. Landon, P.J. Collier, A.F. Carley, D. Chadwick, A.J. Papworth, A. Burrows, C.J. Kiely, G.J. Hutchings, Phys. Chem. Chem. Phys. 5 (2003) 1917–1923.;
- (b) S. Abate, S. Melada, G. Centi, S. Perathoner, F. Pinna, G. Strukul, Catal. Today 117 (2006) 193–198.;
- (c) C. Burato, P. Centomo, M. Rizzoli, A. Biffis, S. Campestrini, B. Corain, Adv. Synth. Catal. 348 (2006) 255–259.;
- (d) C. Samanta, V.R. Choudhary, Catal. Commun. 8 (2007) 73–79.;
- (e) G. Li, J.K. Edwards, A.F. Carley, G.J. Hutchings, Catal. Today 122 (2007) 361–364.;
- (f) J.K. Edwards, A. Thomas, B.E. Solsona, P. Landon, A.F. Carley, G.J. Hutchings, Catal. Today 122 (2007) 397–402.
- [14] R. Hiatt, in: R.L. Augustine, D.J. Trecker (Eds.), Oxidation, Marcel Dekker, New York, 1971, pp. 113–140.
- [15] G. Strukul, in: G. Strukul (Ed.), Catalytic Oxidations with Hydrogen Peroxide as Oxidant, Kluwer Academic Publishers, Dordrecht, 1992, pp. 177–221.
- [16] W. Laufer, R. Meiers, W. Hölderich, J. Mol. Catal. A: Chem. 141 (1999) 215–221.
- [17] Q. Wang, L. Wang, Z. Mi, Catal. Lett. 103 (2005) 161–164.
- [18] P. Mehrotra, X.E. Verykios, J. Catal. 88 (1984) 409–417.
- [19] (a) Imperial Chemical Industries Ltd. Brit. GB 1201086 (1970); Chem. Abstr. 73, 77032.;
- (b) Mitsubishi Chemical Industries Co., Jpn. Tokkyo Koho JP 57015094 (1982); Chem. Abstr. 97, 38842.;
- (c) B.T. Pennington, U.S. Patent US 4,883,889 (1989); Chem. Abstr. 97, 97040.;
- (d) C.P. Cheng, Y.H. Hwang, C.C. Liu, U.S. Patent US 5,223,631 (1993); Chem. Abstr. 1994, 120, 167272.;
- (e) U. Jansen, G. Wiessmeier, Ger. Offen. DE 10024096 (2001); Chem. Abstr. 135, 372153.;
- (f) R.A. Grey, U.S. Patent US 6,441,203 (2002); Chem. Abstr. 137, 185988.;
- (g) U. Müller, L. Lobree, M. Hesse, O.M. Yaghi, M. Eddaoudi, U.S. Patent US 6,624,318 (2003); Chem. Abstr. 139, 278233.;
- (h) G. Paparatto, A. Forlin, G. De Alberti, R. D'Alaisio, P. Tegon, PCT Int. Appl. WO 014297 (2002); Chem. Abstr. 136, 184270.;
- (i) G. Paparatto, A. Forlin, G. De Alberti, R. D'Alaisio, P. Tegon, PCT Int. Appl. WO 014299 (2002); Chem. Abstr. 136, 184272.;
- (j) J.R. Lockemeyer, U.S. Patent US 085,649 (2005); Chem. Abstr. 142, 392824.;
- (k) Y.-Y. Liu, K. Murata, H. Inaba, Jpn. Kokai Tokkyo Koho JP 161208 (2005); Chem. Abstr. 143, 43416.;
- (l) G.-P. Schindler, C. Walsdorff, R. Koerner, H.-G. Goebbel, PCT Int. Appl. WO 000396 (2007); Chem. Abstr. 146, 81755.
- [20] R.A. Sheldon, J.A. van Doorn, J. Organomet. Chem. 94 (1975) 115–129.
- [21] A. Matsuura, Y. Ito, T. Matsuura, J. Org. Chem. 50 (1985) 5002–5004.
- [22] Y. Ito, A. Matsuura, T. Matsuura, Tetrahedron Lett. 25 (1984) 1491–1494.
- [23] E.P. Talsi, V.P. Babenko, V.A. Likhobolov, V.M. Nekipelov, V.D. Chinakov, J. Chem. Soc., Chem. Commun. (1985) 1768–1769.
- [24] E.P. Talsi, V.P. Babenko, A.A. Shubin, V.D. Chinakov, V.M. Nekipelov, K.I. Zamaraev, Inorg. Chem. 26 (1987) 3871–3878.
- [25] H. Mimoun, R. Charpentier, A. Mitschler, J. Fischer, R. Weiss, J. Am. Chem. Soc. 102 (1980) 1047–1054.
- [26] G. Strukul, R. Ros, R.A. Michelin, Inorg. Chem. 21 (1982) 495–500.
- [27] C. Martin, M. Faraj, J. Martin, J.-M. Brégeault, J. Mercier, J. Fillaux, P. Dizabo, J. Mol. Catal. 37 (1986) 201–212.
- [28] M.A. Andrews, C.-W.F. Cheng, J. Am. Chem. Soc. 104 (1982) 4268–4270.
- [29] H. Mimoun, J. Mol. Catal. 7 (1980) 1–29.
- [30] H. Mimoun, Angew. Chem., Int. Ed. Engl. 21 (1982) 734–750.
- [31] M.A. Andrews, T.C.-T. Chang, C.-W.F. Cheng, K.P. Kelly, Organometallics 3 (1984) 1777–1785.
- [32] M.A. Andrews, T.C.-T. Chang, C.-W.F. Cheng, Organometallics 4 (1985) 268–274.
- [33] S. Paraskewas, D. Konstantinidis, Chemiker-Zeitung 102 (1978) 236.
- [34] M.A. Andrews, C.W. Cheng, K.P. Kelly, US 398,508 (1983); Chem. Abstr. 101, 7771.
- [35] A. Heumann, F. Chauvet, B. Waegell, Tetrahedron Lett. 23 (1982) 2767–2768.
- [36] F. Chauvet, A. Heumann, B. Waegell, J. Org. Chem. 52 (1987) 1916–1922.
- [37] M.A. Andrews, K.P. Kelly, J. Am. Chem. Soc. 103 (1981) 2894–2896.
- [38] P.K. Wong, M.K. Dickson, L.L. Sterna, J. Chem. Soc., Chem. Commun. (1985) 1565–1566.
- [39] J. Bussi, A. López, F. Peña, P. Timbal, D. Paz, D. Lorenzo, E. Dellacasa, Appl. Catal. A: Gen. 253 (2003) 177–189.
- [40] P.N. Dyer, Ger. Offen. DE 2746812 (1978); Chem. Abstr. 89, 43091.
- [41] A. Cabrera, A.M. Perez, M. Salmón, N. Rosas, Synth. React. Inorg. Met. Org. Chem. 25 (1995) 1507–1516.
- [42] K. Otsuka, M. Yoshinaka, I. Yamanaka, J. Chem. Soc., Chem. Commun. (1993) 611–612.
- [43] H.-S. Ryang, C.S. Foote, J. Am. Chem. Soc. 102 (1980) 2129–2131.
- [44] A. Atlamsani, E. Pedraza, C. Potvin, E. Duprey, O. Mohammedi, J.-M. Brégeault, C.R. Acad. Sci. Paris, Série II 317 (1993) 757–762.
- [45] N. Fdil, A. Romane, S. Allaoud, A. Karim, Y. Castanet, A. Mortreux, J. Mol. Catal. A: Chem. 108 (1996) 15–21.
- [46] H. Gao, R.J. Angelici, Synth. Commun. 30 (2000) 1239–1247.
- [47] M. Sato, Y. Kobayashi, M. Hiraoka, Jpn. Tokkyo Koho JP 50012406 (1975); Chem. Abstr. 83, 206085.
- [48] (a) M.S. Kharasch, G. Sosnovsky, Tetrahedron 3 (1958) 97–104.;
- (b) H.G. Aurich, Tetrahedron Lett. (1964) 657–658.;
- (c) K. Tanaka, J. Imamura, Chem. Lett. (1974) 1347–1348.
- [49] K. Murata, Y. Liu, N. Mimura, M. Inaba, J. Catal. 220 (2003) 513–518.
- [50] Y. Liu, K. Murata, M. Inaba, Chem. Commun. (2004) 582–583.
- [51] Y. Liu, K. Murata, M. Inaba, N. Mimura, Appl. Catal. A: Environ. 58 (2005) 51–59.
- [52] Y. Liu, K. Murata, M. Inaba, Green Chem. 6 (2004) 510–515.
- [53] Y. Liu, K. Murata, M. Inaba, Chem. Lett. 35 (2006) 436–437.
- [54] For reviews on Pd-catalysed oxidations of alcohols, see:
- (a) J. Muzart, Tetrahedron 59 (2003) 5789–5816.;
- (b) B.M. Stoltz, Chem. Lett. 33 (2004) 362–367.;
- (c) S. Stahl, Angew. Chem. Int. Ed. 43 (2004) 3400–3420.;
- (d) M.E. Sigman, D.R. Jensen, Acc. Chem. Res. 39 (2006) 221–229.
- [55] Y. Liu, K. Murata, T. Hanaoka, M. Inaba, K. Sakanishi, J. Catal. 248 (2007) 277–287.
- [56] R. Nagata, T. Matsuura, I. Saito, Tetrahedron Lett. 25 (1984) 2691–2694.
- [57] M.J.Y. Chen, J.K. Kochi, J. Chem. Soc., Chem. Commun. (1977) 204–205.
- [58] R. Nagata, I. Saito, Synlett (1990) 291–300.
- [59] I. Saito, T. Mano, R. Nagata, T. Matsuura, Tetrahedron Lett. 28 (1987) 1909–1912.
- [60] M. Roussel, H. Mimoun, J. Org. Chem. 45 (1980) 5387–5390.
- [61] R. Neumann, A.M. Khenkin, Inorg. Chem. 34 (1995) 5753–5760.
- [62] See also:
- (a) T. Schiffer, G. Oenbrink, B. Krebs, E. Droste, M. Piepenbrink, G. Vollmer, Eur. Pat. Appl. EP 1205474 (2002); Chem. Abstr. 136, 385888.;
- (b) N. Mizuno, Y. Sumida, K. Yonehara, M. Wada, M. Urata, PCT Int. Appl. WO 072257 (2002); Chem. Abstr. 137, 248099.
- [63] A. Kumar, Catal. Commun. 8 (2007) 913–916, and cited references.

- [64] M. Nishida, A. Torii, Jpn. Kokai Tokkyo Koho JP 187,792 (2001); Chem. Abstr. 135, 92546.
- [65] Y.-J. Cho, K.-C. Kim, J.-H. Jeong, Y.-C. Park, M.-K. Do, Bull. Korean Chem. Soc. 16 (1995) 211–214; Chem. Abstr. 123, 32715.
- [66] H. Jiang, Q.-D. Qiao, H. Gong, Pet. Sci. Technol. 17 (1999) 955–965; Chem. Abstr. 132, 78339.
- [67] M.B. Francis, E.N. Jacobsen, Angew. Chem., Int. Ed. 38 (1999) 937–941.
- [68] B.S. Lane, M. Vogt, V.J. DeRose, K. Burgess, J. Am. Chem. Soc. 124 (2002) 11946–11954.
- [69] B.A. Allal, L.E. Firdoussi, S. Allaoud, A. Karim, Y. Castanet, A. Mortreux, J. Mol. Catal. A: Chem. 200 (2003) 177–184.
- [70] E. Gusevskaya, P.A. Robles-Dutenhefner, V.M.S. Ferreira, Appl. Catal. A: Gen. 174 (1998) 177–186.
- [71] C. Chevrin, J. Le Bras, F. Hénin, J. Muzart, Synthesis (2005) 2615–2618.
- [72] E. Thiery, C. Chevrin, J. Le Bras, D. Harakat, J. Muzart, J. Org. Chem. 72 (2007) 1859–1862.
- [73] J. Wahlen, D.E. De Vos, P.A. Jacobs, Org. Lett. 5 (2003) 1777–1780.
- [74] According to literature, it is not possible to isolate 2-(3-methyloxiran-2-yl)phenol:
(a) S.W. Tinsley, J. Org. Chem. 24 (1959) 1197–1199;
(b) A. Lattanzi, A. Senatore, A. Massa, A. Scettri, J. Org. Chem. 68 (2003) 3691–3694.
- [75] J.-Q. Yu, E.J. Corey, Org. Lett. 4 (2002) 2727–2730.
- [76] G.-X. He, T.C. Bruice, J. Am. Chem. Soc. 113 (1991) 2747–2753.
- [77] A. Bravo, H.R. Bjørsvik, F. Fontana, L. Liguori, F. Minisci, J. Org. Chem. 62 (1997) 3849–3857.
- [78] F. Minisci, F. Fontana, S. Araneo, F. Recupero, S. Banfi, S. Quici, J. Am. Chem. Soc. 117 (1995) 226–232.
- [79] This reactivity of stilbenes and styrene is reminiscent to that we previously observed using *t*-BuOOH under Cr^{VI} catalysis:
J. Muzart, A. N'Ait Ajjou, New. J. Chem. 18 (1994) 731–736.
- [80] T. Nishimura, T. Onoue, K. Ohe, J. Tateiwa, S. Uemura, Tetrahedron Lett. 39 (1998) 4359–4362.
- [81] W.F. Brill, N. Indictor, J. Org. Chem. 29 (1964) 710–713.
- [82] J.D. Koola, J.K. Kochi, J. Org. Chem. 52 (1987) 4545–4553.
- [83] Surprisingly, the reported scheme showed a trans-peroxypalladation [75] instead of the usually accepted cis-insertion of CF₃CO₂PdOO*t*-Bu into the C=C bond [25,30].
- [84] J. Muzart, J.-P. Pête, A. Riahi, J. Organomet. Chem. 331 (1987) 113–119.
- [85] A. Fusi, R. Ugo, F. Fox, A. Pasini, S. Cenini, J. Organomet. Chem. 26 (1971) 417–430.
- [86] W.F. Brill, J. Am. Chem. Soc. 85 (1963) 141–145.
- [87] L.L. Csányi, K. Jáky, Phys. Chem. Chem. Phys. 3 (2001) 2018–2024.
- [88] K. Konishi, F. Xu, Y. Murakami, Chem. Lett. 35 (2006) 476–477.
- [89] E.H. Kim, D.I. Kim, H.S. Lee, H.G. Na, J.C. Byun, J.H. Choi, Y.C. Park, Polyhedron 26 (2007) 85–92.
- [90] For insights into the possible intermediates leading to the regeneration of active Pd^{II} species with oxygen, see:
(a) J. Muzart, Chem. Asian J. 1 (2006) 508–515;
(b) K.M. Gligorich, M.S. Sigman, Angew. Chem. Int. Ed. 45 (2006) 6612–6615.