Modern Methods for the Epoxidation of α- and β-Pinenes, 3-Carene and Limonene

O. V. BAKHVALOV, V. V. FOMENKO and N. F. SALAKHUTDINOV

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 9, Novosibirsk 630090 (Russia)

E-mail: fomenko@nioch.nsc.ru

Abstract

The present review is emphasized on chemical aspects of epoxidation, environmental safety of promising methods for processing such a renewable raw material as terpenes. Various epoxidizing systems are considered, first of all those allowing one to perform catalytic epoxidation of terpenes, as well as their prospective value for commercial introduction. The review has included the materials published within the period from 1988 to 2008. For the convenience of comparing various epoxidizing systems and of choosing optimum conditions for the process carrying out, all the data are listed to form common tables.

Key words: terpen, epoxidation, green chemistry, renewable raw material, oxidation

Contents

INTRODUCTION

The epoxidation of olefins represents a convenient way to activate and fuctionalize them [1–5] which quite often serves as the first stage of various kinds of industrial production [6–9]. A plenty of works, including a number of the reviews performed for the last decade [3, 10–12] devoted to this process are available from the literature. The authors of the monograph [10] considered epoxidation of alkenes in a particularly academic theoretical aspect wherein terpenes were out of consideration. There are transformations discussed in this book those proceed under the influence of individual agents enriched with active oxygen on olefins, instead of real epoxidizing systems. The review is useful for understanding the mechanisms of epoxidation, but it is less interesting from the standpoint of choosing the conditions in order to carry out a preparative synthesis of terpene epoxides. An extensive review [3] is devoted mainly to oxidation reactions of compounds from various classes. In the section devoted to the epoxidation, terpenes figured as initial compounds only for two reactions among several tens of reactions presented. The authors of [12] listed a number of catalytical epoxidation systems including hydrogen peroxide. However, only one terpene was used among initial alkenes. A similar approach is described also in a very brief review [11].

Nowadays the success in the field of fine organic synthesis of terpenoids is obvious. From the theoretical point of view it is quite possible that combining known methods of organic synthesis one could obtain almost any known or potentially interesting from the practical standpoint of view terpenoids. On the other hand, provided putting a question concerning profound

processing of significant amounts of phytogenous raw material (for example, turpentines, by-produced in the manufacture of cellulose, or limonene by-produced in obtaining juices of citrus plants) the following disadvantages of known methods for the conversion of terpenoids are revealed to be obvious:

1. A necessity to use great volumes of expensive and frequently hazardous reagents in order to perform the synthesis. These circumstances cause, in particular, the formation of hazardous and difficult to recover waste in the amounts several times exceeding the volumes of the obtained product [13].

2. Due to a low selectivity of the reactions one should carry out a careful and expensive preparation of reagents and/or separation of complex mixtures of products.

3. A low yield of target products caused by manifold reactivity of natural compounds.

Solving practical problems, chemists confront either with one of these circumstances (for example, performing the process with a high selectivity is possible, but it demands high expenses and practically non-feasible, hazardous reactants) or with their combination when even the application of modern "laboratory" methods of organic synthesis can not provide obtaining the products with a reasonable yield. As a result we have an essential difference in the price of the products of the general and fine organic synthesis based on the one hand on the products of petrochemistry, and on the other hand on the products of dendrochemistry.

It is obvious that the development of "usual" non-catalytic methods of organic synthesis in the field of dendrochemistry cannot change the situation developed. In this connection the catalytic epoxidation of terpenes could be considered to be one of the most promising directions in the field of using a renewable phytogenous raw material.

The present review considers the papers concerning the epoxidation of available naturally occurring terpenes (α- and β-pinenes, 3-carene and limonene) published within the period from 1988 to 2008. During last decade, publications concerning biochemical epoxidation of terpenes began to appear [14–20] those will be also considered below. However, the main attention will be given to chemical methods for epoxidation. The effects of enantioselectivity and diastereoselectivity of oxidizing systems under use are not discussed in the present work.

Our work is intended to help researchers and technologists in choosing from the literature data some rational conditions for practical epoxidation of terpenes those are suitable for scaling this process up to industrial synthesis of oxiranes.

SOME GENERAL LAWS FOR EPOXIDATION OF TERPENES

As much as 24, 41, 119 and 129 works, respectively, are devoted to the problems of the synthesis of β-pinene, 3-carene, limonene and α-pinene epoxides in the literature. Such a ratio is to a certain extent reflecting the availability of the terpenes listed their readiness for epoxidation and practical importance of epoxides obtained. The following order for the ability of terpenes to be oxidized [21] is known: 3-carene > α-pinene > limonene > β-pinene.

However, the data we have gathered demonstrate that the capability of terpenes to exhibit the formation of the oxirane cycle depends not only on the structure of an initial compound, but also on the conditions this reaction is carried out. An essential role is played, for example, by the size of an attacking complex (a catalyst with an epoxidizing agent [22]), by the nature of the epoxidizing agent [23], by solvent [24] and other conditions of the process. For example, for the epoxidation by *t*-BuOOH and cumene hydroperoxide the decrease in activity for both epoxidizing agents can be presened by the following series: cyclohexene > limonene > α-pinene > β-pinene > camphene.

The absolute values of the conversion level in the reactions of *t*-BuOOH oxidation by cumene hydroperoxide [25] and by some other oxidizers are presented in Table 1.

One can see that to establish a universal scale for the reactivity of olefins in the reaction of double bond oxidation with the formation of oxiranes is impossible. Hence, the statement occurring in the literature that the double bond in this cycle is much more reactive than a double bond in a chain or an isolated double bond [31] (which is caused by a somewhat lower entropy loss in a cyclic molecule) is valid only for a limited number of epoxidation variants. It is

TABLE 1

Comparative reactivity of some terpenes in the reaction of epoxidation

Epoxidation conditions	Terpene	Conversion level, %	Selectivity, %	Yield, %	Ref.
O_2, $Ni(acac)_2$, Me_2CHCHO	α-Pinene	100	93	–	[26]
	Limonene	100	81	–	
	3-Carene	97	90	–	
O_2, Ru complex containing cymol and 1,2,4-triazepine, Me_2CHCHO	α-Pinene	100	98	–	[27]
	Limonene	100	91	–	
	3-Carene	96	98	–	
60 % H_2O_2, Al_2O_3	α-Pinene			69	[28]
	Limonene			83	
	3-Carene			87	
35 % H_2O_2, Me_3ReO_3, pyridine	α-Pinene	100	86	80	[1]
	Limonene	100	90	90	
	β-Pinene	98	89	82	
O_2, Co salen complex, Me_2CHCHO	α-Pinene			70	[29]
	Limonene			54	
	3-Carene			48	
	β-Pinene			64	
30 % H_2O_2, DCC, cationite	α-Pinene			73	[30]
	Limonene			64	
	β-Pinene			48	

contradicted, for example, in [32] where it was demonstrated that citral and linalool are readily epoxidized, whereas the yield of α- and β-pinene amounts to 15 % only.

The latter is caused by a spatial hindrance for the attack of double bonds by a bulky diatomic Mn complex. A surprising dependence of epoxidation results on the reaction conditions (mainly on the nature of a polyoxomethylate catalyst under use) has been demonstrated in [33], whose authors obtained 8,9-epoxide from *R*(+)-limonene with the yield of 89 % under soft conditions. With the use of other catalysts the formation of this compound under direct epoxidation conditions either did not occur or its yield in the mixture with others isomers did not exceed 30–35 %.

A law manifested by the fact that the epoxidation rate increases in the presence of electron accepting groups in the source of active oxygen as well as of electron donating groups in alkene [34, 35] is considered to be more universal. It should exhibit in the cases when the mechanism of electrophilic oxygen addition to the double bond is realized. However, the works considered in the review demonstrate a much more complicated, ambiguous and not conclusively established picture of oxiranes formation. Three types of mechanisms are considered to be possible for epoxidation reactions such as a catalytic oxygen transfer to the double bond, a free-radical mechanism and a Prilezhaev reaction for the case when it is performed with peracids.

MECHANISMS FOR THE INTERACTION OF TERPENES WITH EPOXIDIZING AGENTS. THE FEATURES OF SOME EPOXIDATION PROCESSES

The reactions of active oxygen addition to the double bonds of terpenes use to proceed both in the presence of catalysts, and without them. The catalysis can be of both homogeneous and heterogeneous nature. Recently there is a tendency to use the second variant is mainly observed, whose basic advantage consists in the potentiality of a repeated use of a catalyst. A number of compounds (Tables 3–6) are used as a source of active oxygen, but much more often the latter represents hydrogen peroxide or molecular oxygen (air) (Table 2).

TABLE 2

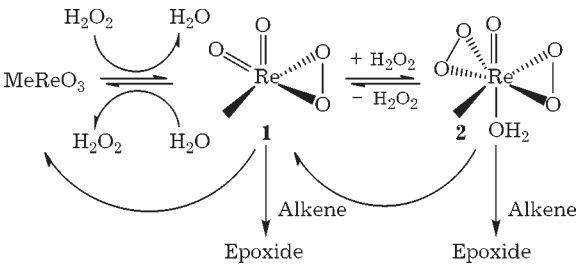
Main components of the systems epoxidizing terpenes

Initial compound	Overall number of publications	Number of publications whose authors use:		
		catalysts	H_2O_2	O_2
β-Pinene	24	16 (67)	13 (54)	4 (17)
3-Carene	41	29 (71)	28 (68)	7 (17)
Limonene	119	97 (81.5)	46 (39)	24 (20)
α-Pinene	129	106 (82)	43 (33)	40 (31)

Note. The percentage with respect to the total number of publications is specified in brackets.

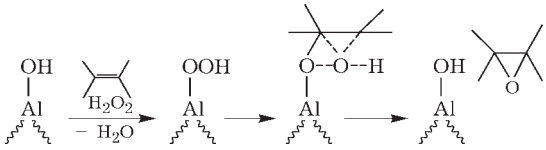
It should be noted that the contribution of catalytic processes with the use of molecular oxygen as an oxidizer increases in the order of β-pinene, 3-carene, limonene, α-pinene.

The discovery of the catalytic properties of Me_3ReO_3 (MTO) in the reactions of epoxidation became a remarkable milestone in this research field [12]. Many alkenes can be epoxidized in the presence of this substance under the action of hydrogen peroxide at a room temperature.



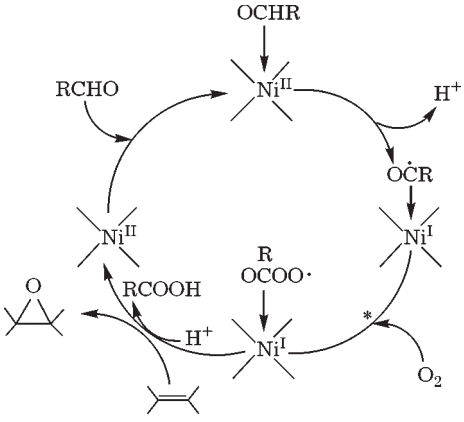
Rhenium being heptavalent in the compound Me_3ReO_3, activates hydrogen peroxide through the formation of η^2-peroxo species **1** and **2**. The structure of compound **2** is confirmed by the data of crystallographic analysis; the presence of species **1** and **2** is proved with the use of NMR spectroscopic methods [12]. As complex compounds with nitrogen-containing ligands are formed from MTO its reactivity increases. In order to prevent these ligands from washing away the MTO is introduced into the structure of a polyvinylpyridine resin [36] or its complex is incapsulated into polystyrene [37]. Thus a heterogeneous catalyst is obtained suitable in order to use it repeatedly.

Aluminium oxide have appeared a quite good catalyst of epoxidation reaction, in particular basic one as well as that obtained according to the method of sol-gel technology [38]. Its cheapness, availability and ecological compatibility have caused interest in detailed studies on potentialities of this catalyst application [39, 40]. The mechanism proposed for epoxidation is as it follows:



Much the same technological parameters are reached with the use anhydrous hydrogen peroxide and its) 60 % solution for epoxidation at 60–70 °C. In the latter case the process requires for water evaporation from reaction the mixture using a Dyne–Stark apparatus. Aluminium oxide can be used use three times, further with the conservation or even increase in the selectivity of limonene epoxidation the conversion level is considerably reduced.

Complexes of transition metals with β-diketones are widespread epoxidation catalysts. The authors of [41] studied the mechanism and kinetics for the epoxidation of alkenes in the presence of $Ni(acac)_2$, isobutyl aldehyde and molecular oxygen (usual conditions for the catalysts mentioned). A simplified picture of process is presented below:

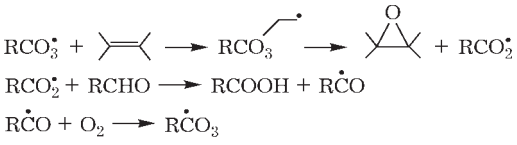


* Reaction rate determining stage.

The authors of [41] have concluded that the epoxidation reaction occurs at a ratio aldehyde : alkene ≥ 2, whereas the first important stage is presented by aldehyde coordination with the nickel complex. The role of this complex consists in promoting the hydrogen atom abstraction from aldehyde and in the acceleration of oxidation reaction. From the aforementioned Figure one could see both radical and non-radical reactions to occur within the cycle, however the authors of [41] considered the nature of the process to be radical one and basing on kinetic studies came to the conclusion, that the reaction rate of the process does not depend on the concentration of an initial substance.

Copper salts can operate as active oxidation (epoxidation) catalysts. The authors of [35] have proposed a reactivity series for similar compounds those they have obtained through the oxidation of adamantine by molecular oxygen in the presence of acetaldehyde. The experiments which they carried out in order to find out the oxidation mechanism for substituted toluenes in the presence of $Cu(OH)_2$, have demonstrated that there are reactive intermediates such as $Cu^{3+}-O^{\bullet}$ or $Cu^{4+}=O$ formed. The data obtained are mainly strengthening the case for radical mechanisms.

Compounds containing cobalt such as CoNaY, $Co(NO_3)_2$, $PW_{11}Co$, CoW_{12}, Co phtalocyanine [42] are also efficient catalysts in the presence of oxygen and aldehyde. The authors of this work considered the epoxidation with Co^{2+} compounds is a free-radical process initiated by such adducts as $Co^{3+}-O-O$. The latter react with aldehydes, which results in $RCO_3^{\bullet}$ radical formation with the participation of oxygen of at the final stage of the process.



Under the conditions specified the reactivity with the repeated use is exhibited also by cobalt polyoxometallates, applied onto modified mesoporous silicate matrices. The nature of a matrix and its treatment influence the catalyst activity [43].

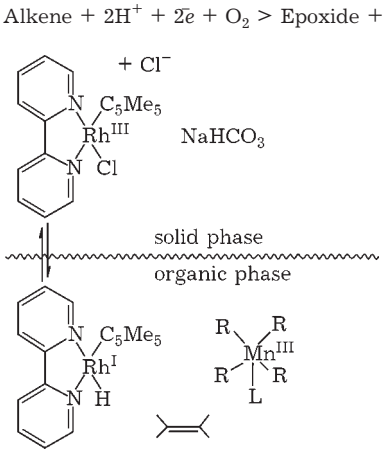


Fig. 1. Schematic presentation of a catalytic system, which illustrates the role of $[Rh(C_5Me_5)bipyCl_2]$ complex as a phase-transfer catalyst. C_5Me_5 – pentamethylpentadiene.

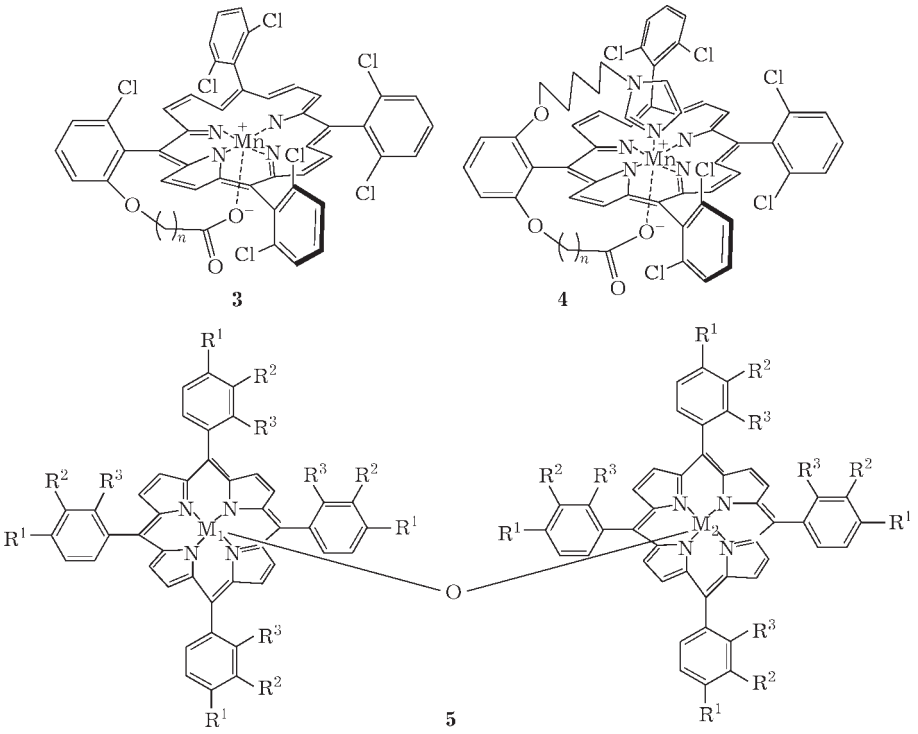
The greatest number of works (18 publications) is devoted to the studies on the catalytic system based on Mn porphyrin. This system is modified through the introduction of aromatic substituents into the positions 5, 10, 15, 20 of the porphyrin ring. The best results were obtained in the case of porphyrins with phenyl substituents. The metal of the porhyryn complex is bound with axial ligands such as chlorine, acetyl group, nitrogen-containing compounds (N-alkylimidazole). A more complicated two-phase system was also proposed with the reductive activation of oxygen [44] (Fig. 1).

The complication of porphyrin catalysts is expressed also in the introduction of additional substituents (Scheme 1, structures **3**–**5**).

Catalysts are also synthesized those have the structures with the cavities located lower than the porphyrin ring plane wherein axial ligands (nitrogen-containing heterocycles) can be placed. These ligands could influence the results of epoxidation [45].

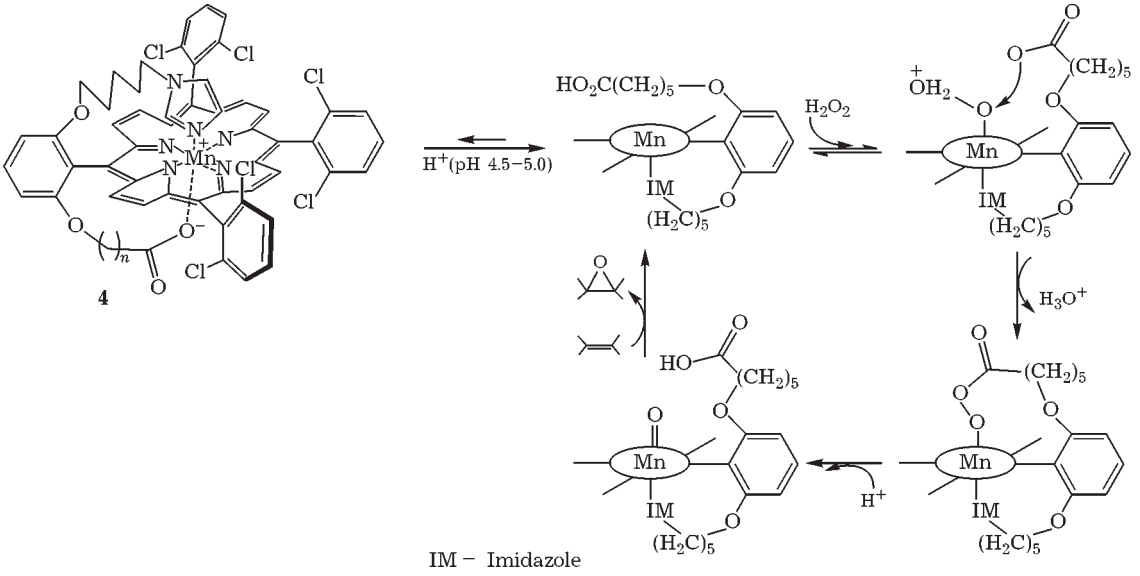
The epoxidation mechanism hypothesized is demonstrated in Scheme 2 [46].

Methods for immobilizing the catalysts under discussion are also proposed, for example, onto zeolite Y [47], polystyrene [48], modified SiO_2 [49]. All the modifications of Mn porphyrins are able to catalyze to a greater or lesser extent the reactions of allyl oxidation of terpenes.



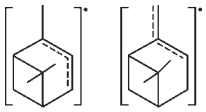
$M_1 = M_2 = Mn$; $R_1 = NO_2$; $R_2 = R_3 = H$.

Scheme 1.



Scheme 2.

A catalytic system based on Fe porphyrin is of limited occurrence. This system was subjected to a detailed investigation by the authors of [50]. The role of the catalyst could consists, to all appearance, in the initiation of a chain reaction *via* hydrogen abstraction from terpene and decomposition of the hydroperoxide or hydroperoxyl radicals formed from radicals **6** and **7** and molecular oxygen.



6 **7**

The radicals form with porphyrins a cation-radical species according to the equation

$(P)Fe^{3+}X + ROO(H) \rightarrow (P)^{+\bullet}Fe^{4+}(=O)X + RO(H)$

This intermediate species is considered to be responsible for the epoxidation:

$(P)^{+\bullet}Fe^{4+}(=O)X + \text{Alkene} > (P)^{+\bullet}Fe^{3+}X + \text{Epoxide}$

8

The authors of [51] have found out that with the increase of electron donating effect of substituents in the phenyl fragments of porphyrin complexes their catalytic activity falls. They proposed the relationship $\ln k = 1.2168\sigma - 7.9968$ for Mn porphyrin complex, and the relationship $\ln k = 0.625\sigma - 8.2426$ for Fe porphyrin complex, where k is a the reaction rate constant, and σ is the Hammet constant for a substituent.

Cobalt porphypin catalysts under aerobic conditions in the presence of aldehydes are characterized as universal ones: they are able to oxidize alcohols, benzyl compounds, arenes, alkenes, alkanes [52, 53]. In this case the reactions proceed via cobalt oxo species similar to intermediate species **8**. In the publications included in the aforementioned reviews, among all the set of terpenes considered only limonene was entered into reaction with the Co porphyrin catalyst The authors investigated the influence of the substituent nature in the aromatic fragments of porphyrins upon the results of the reaction and noted that electron donating substituents cause an increase in the activity of catalysts. Aldehydes, especially 2-methylpropanal, perform the function of reductive oxygen activation.

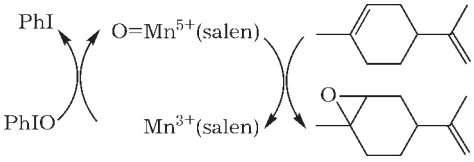
The consideration of the features of metal porhyrin catalysts would be logically completed with the comparison of their activities depending on the nature of metal. This could be expressed by the following order of conversion level values for α-pinene under the conditions mentioned above [54]: $TPPMn^{3+}Cl > TPPCo^{3+}Cl > TPPFe^{3+}Cl > TPPCu^{2+} \approx TPPNi^{2+} \approx TPPZn^{2+}$ (TPP standing for tetraphenylporphyrin).

The dependence presented is inherent in the first three members of the series and coincides with that for the reactions of limonene epoxidation [55]. The authors of this paper have revealed the activation of limonene conversion with the use *t*-BuOOH instead of NaOCl as an oxidizer and methylene chloride instead of acetonitrile and ethyl acetate as a solvent.

Manganese compounds are much more preferable than others also due to the cheapness and non-toxicity of this metal.

A great many of works is devoted to metal porphyrins. Among several books a monograph [56] where one of the sections is devoted to the epoxidation of alkenes (rather than terpenes) by some people metal porphyrins has a relevancy to the topic of the present review.

Another group of composite complex catalysts with transition metal as a central atom is formed by Mn- and Co-salen complexes (in the articles for 2006–2007 they are referred to as "salophen complexes"). The mechanism of epoxidation by them is identical and similar to that occurring in the reaction of epoxidation by porphyrins. To all appearance, during the oxidation a radical such as $M-O-O^{\bullet}$ is formed (it is demonstrated by ESR method) to convert into an oxometallic intermediate species (salen) M=O which transfers oxygen to the double bond of olefin [57].



An epoxidizing agent depicted in the Scheme is typical alongside with $PhIO_4$, $NaIO_4$ and O_2 for salen complexes (the use of hydrogen peroxide is inefficient). Salen complex catalysts in the reaction of epoxidation exhibit the following features:

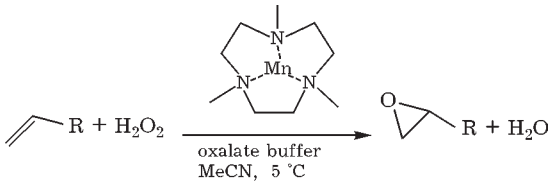
1. Simultaneously with epoxidation the allyl oxidation of terpenes and the formation of alcohols and ketones are observed to occur. These processes are of free-radical nature.

2. The reductive activation of oxygen can be realized with various carbonyl compounds.

3. The direction and results of the process are to a considerable extent depending on the structure of a salen complex.

A number of immobilized salen complexes have been obtained on Dowex MsCl [58], on modified macroporous zeolites [59], on silica gel, polystyrene, MCM-41, montmorillonite (see Tables 3–6). In some of papers listed a comparison of the results was carried out for the epoxidation with the use of immobilized salen catalysts and with the use of homogeneous media. The former variant resulted in improving the manufacturability and selectivity of the process, as well as in growing the yield of epoxide, whereas the reaction rate and the productivity of catalyst decreased. The catalyst linkage with a support can be realized through imidazole or 1,4-phenylenediamine, as well as *via* the incapsulation within the pores of zeolite.

Rather high activity in the epoxidation of some terpenes is exhibited by Mn complex with trimethyltriazacyclononane. The introduction of the oxalate buffer in the system prevents hydrogen peroxide from decomposition and allows one to epoxidize terminal double bonds successfully [11].



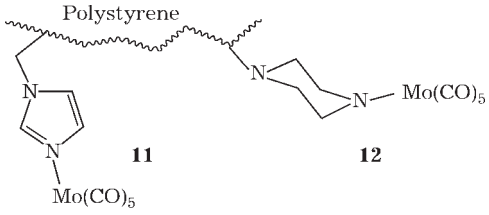
This catalyst can be immobilized onto silica gel [60]. The disadvantages of the catalyst should be considered to consist in its ability to initiate the formation of diols, as well as campholenic aldehyde (from α-pinene).

The selectivity of epoxidation for alkenes of different structure as well as mainly cyclic alkenes and limonene as compared to α-pinene is inherent also in dioxomolibdenium complex catalysts, such as compounds **9–10a** (Scheme 3).

In this case the reaction with α-pinene results in the formation of many by-products, too.

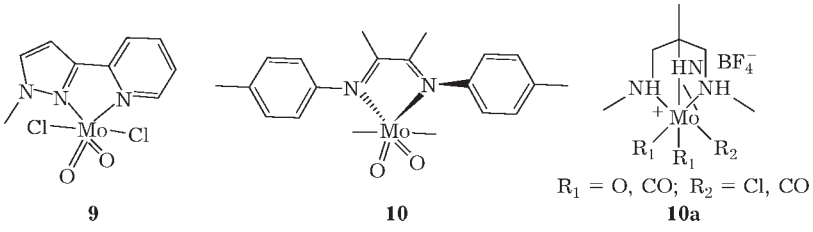
Several works were devoted to the combination of Mo oxides with silicates. Worthy of interest is paper [61] whose authors combined mesoporous silicates (MCM-41, SBA-15) and amorphous porous silicon dioxide with molybdenum oxides in single-reactor synthesis and then carried out comparative studies and tests of the samples obtained. All the varieties of molybdenum silicates almost equally catalyze the reaction of limonene epoxidation with *t*-BuOOH, whereas in the case of using grinded granules (especially precipitated silicon dioxide) the efficiency of catalysts grows in comparison with the mesoporous silicate samples.

Molybdenum carbonyl represents an interesting variety of molybdenum catalysts. The compound is fixed on cross-linked polystyrene via an imidazole or piperazine spacer (fragments **11** and **12**).



Such catalysts demonstrate a high efficiency under repeated use. In this case the authors of all the published works used *t*-BuOOH as an oxidizer (see Tables 3–6).

Binuclear Mn complex $[LMnO_3MnL](PF_6)_2$ **13** described for the first time in 1988, to all appearance, is convenient in using for the technical purposes, for example, for bleaching spots; it is interesting from the theoretical standpoint due to an unprecedentedly small (2.296 Å) distance between Mn atoms inherent in this complex (to compare: the interatomic Mn–Mn distance in the molecule $Mn_2(CO)_{10}$ amounts to 2.93Å).



Scheme 3.

TABLE 3

Main conditions and results for α-pinene epoxidation

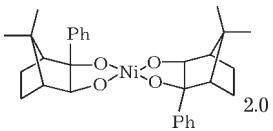
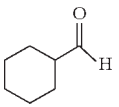
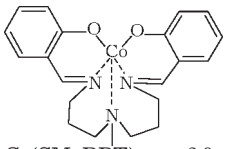
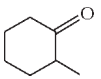
No.	Epoxidizing agent	Catalyst	Auxiliary reagents, co-catalysts	T, °C	Reaction time, h	Conversion level, %	Selectivity, %	Yield, %	Ref.
1	2	3	4	5	6	7	8	9	10
1	40 % MeCOOOH	Phase transfer catalyst	Acid scavenger	10–20	3–5			95	[79]
2	35 % H_2O_2 230	MTO 0.5	Pyridine, 42	20	2.3	100	86	90	[1]
3	35 % H_2O_2 200	$[PW_4O_{24}](C_8H_{17})_3NCH_3$ 1.0	$H_2NCH_2H_2PO_3$ 2.0, $Na_2WO_4 \cdot 2H_2O$ 3.0, NaOH up to pH 4.2	60	1	83	91	76	[80]
4	50 % H_2O_2	$NaWO_4$	QAS			100	94	94	[81]
5	30 % H_2O_2 270		DCC 20, gas – N_2	25	24			83	[82]
6	30 % H_2O_2 120	Mesoporous hybrid $[(MeO)_3SiCH_2]_2$ + $(Me)_4NOH$ + NaOH + H_2O 2.7 mg per 1 mmol of olefin		55	5	up to 23	>99	~23	[83]
7[1]	O_2	 2.0	Me_2CHCHO 300	25	0.5	100	93	93	[26]
8	O_2	Pr compound, 1 mass %	$MeCH_2CHO$ 140	30–60	8	92	73	67	[84]
9	30 % MeCOOOH 110		Anhydrous MeCOONa 154	25	2			82	[85]
10[2]	35% H_2O_2 2000	$MnSO_4$ 0.2	Me_4NHCO_3 100	25	3	53			[69]
11	40% MeCOOOH 100		50 % NaOH up to pH 7	20	1.5	83	~100	~84	[86]
12	O_2	$Cu(OH)_2$ 1.0	 300	25	17	100	84	84	[35]
13	O_2	 Co(SMeDPT) 2.0	 1413	75	6			67	[87]

TABLE 3 (Continued)

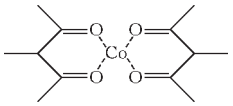
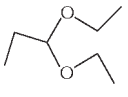
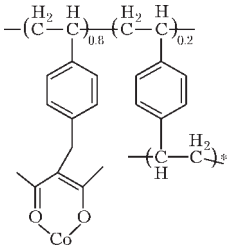
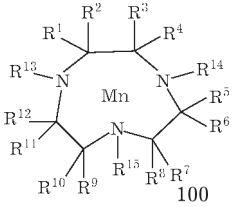
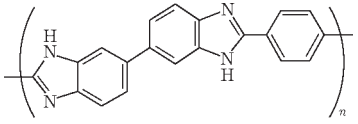
1	2	3	4	5	6	7	8	9	10
14	O_2	 2.0	 4119 Zeolite 4A	45	20	96	97	93	[88]
15	MeCOOOH							89	[89]
16	O_2	 2.4 Co	Me_2CHCHO 200	25	6	97	97	94	[90, 91]
17[3]	5 % H_2O_2 170	 100 R^1–R^{12}, H, various groups R^{13}–R^{15}, H, alkyl, aryl, heteroaryl		25	3			27	[92]
18	O_2		Me_3CCHO 400	25	4	95	95	90	[93]
19	*t*-BuOOH 100	$CuCl_2$	$(n\text{-Bu})_4NBr$	25	14	18	78	14	[73]
20[4]	O_2	$CoBr_2$ 0.15	Pyridine	50	22	~53			[75]
21	O_2	$Ni(acac)_2$, bound with PBI polymer  1.0 Ni	Me_2CHCHO 300	25	4	100	88	88	[94]

TABLE 3 (Continued)

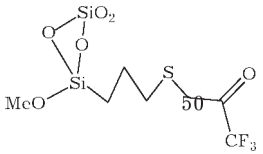
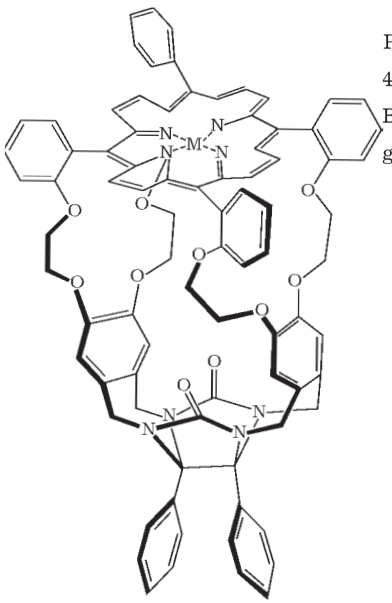
1	2	3	4	5	6	7	8	9	10
22	15 % H_2O_2 200	Mixture of $R_3^{3+}(PW_{12}O_{40})^{3-}$, where $R = \pi C_5H_5N(CH_2)_{15}Me$ + Ph_3SiOEt + $Me_2NCH(OCH_2Ph)_2$ 0.5	Gas − N_2	70	2			92	[95]
23	OKCOH ($2KHSO_5$ + $KHSO_4$ + K_2SO_4) 210		K_2CO_3 870	25	0.1			>98	[96]
24	NaOCl 96	 M = Mn(III)Cl 0.4	Pyridine 04 or 4-*tert*-Bu-pyridine 0.2 Bu_4NCl 0.8 gas − N_2	25	3			81	[97]
25[5]	O_2	Co^{2+} salen incorporated into polyaniline, 6 mg per 1 mmol of olefin	Me_2CHCHO 300	20	4			82	[98]
26	O_2		Na_2CO_3	100	0.7			30	[72]

TABLE 3 (Continued)

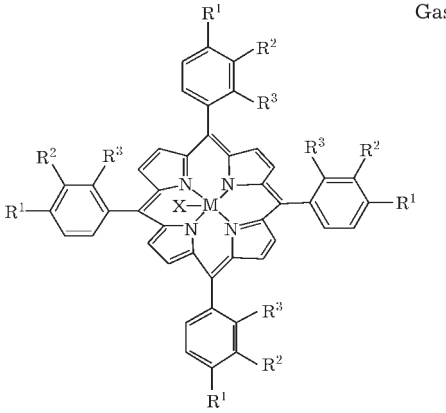
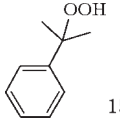
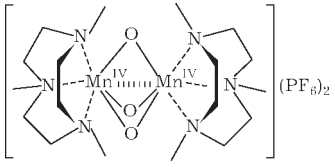
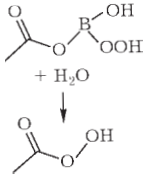
1	2	3	4	5	6	7	8	9	10
27[6]	NaClO	 M = Mn, R_1 = NO_2, R_2 = R_3=H, X = AcO, 0.0095 mg per 1 mmol of olefin	Gas − N_2 or Ar	70	2	90	50	45	[99]
28	 150	Mesoporous material such as MCM-41with formula of $SiO_2 \cdot xTiO_2 \cdot nS$; x = 0.0001−0.5, S is an organic compound		70 70	0.5 8	49 60.5	84 51	41 31	[76]
29	30 % H_2O_2 520	 16	MeCOOH 100	25	1			~10	[22]
30[7]		MnAlPO-5 7.0		65	1	26			[100]

TABLE 3 (Continued)

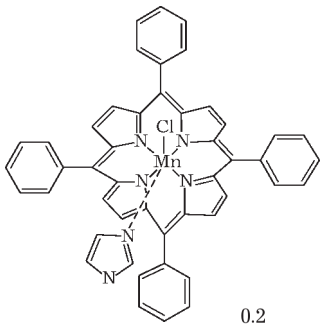
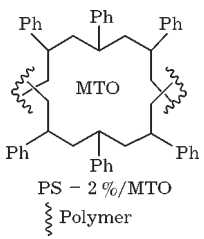
1	2	3	4	5	6	7	8	9	10
31	30 % H_2O_2 4000	$MnSO_4$ 1000	$CO(NH_2)_2$ 2080 $NaHCO_3$ 30	25	9	91	93	85	[101]
32	O_2	 0.2	Irradiation with light at 380 nm < λ < 750 nm	40	16			30–33	[102]
33	PhIO	Mn^{3+} salen Cl 1.0	Gas – N_2 or Ar	25	16	50–60	~36	20	[103]
34	*t*-BuOOH 30 or 30 % H_2O_2 120	Mesoporous Ti-MCM-41 2.7 mg per 1 mmol of olefin		55 55	5 5	11 6	100 100	11 6	[104]
35	30 % H_2O_2 1000	$MnSO_4$ 10	0.2 M $NaHCO_3$ sol., pH 8	25	16			54	[105]
36	O_2	Fe_2O_3 1.0	Benzaldehyde	25	17.5	100	90	90	[106]
37[8]	30 % H_2O_2 520	WO_3 1.7	H_3BO_3 1.0 1.0 NaOH 4.0 $(C_8H_{17})_3MeNHSO_4$ 1.0	70	4			19	[107]
38	30 % H_2O_2 120	 PS – 2 %/MTO Polymer 150 mg per 1 mmol of olefin		25	1.5	>98	100	>98	[36]

TABLE 3 (Continued)

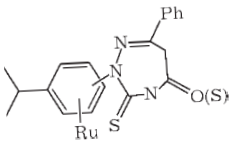
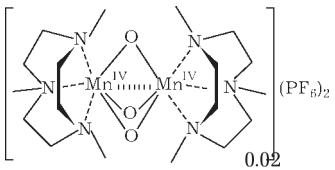
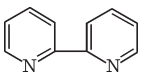
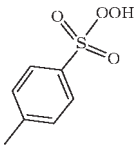
1	2	3	4	5	6	7	8	9	10
39	O_2	 0.15	Me_2CHCHO 308	25	0.5	100	98	98	[27]
40[9]	60 % H_2O_2 200	Al_2O_3 subacidic 49	$(C_4H_9)_2O$ 10 Gas − N_2	~77	4			69	[28]
41	30 % H_2O_2 520	 0.02		25	0.25	10	97	10	[108]
42	30 % H_2O_2 200	$HPO_4W_2O_2(\mu\text{-}O_2)_2(O_2)^{2-}$ $(n\text{-}C_6H_{13})_4N^+$ 1.0 by W		20	3	30	98	29	[109]
43			Gas − Ar	−5... 0	2	100	~93	92−95	[110]
44	O_2	$Ni(acac)_2$, impregnated into clay K-10 (Clayniac) 10 mg per 1 mmol of olefin	Me_2CHCHO 220	25	16	100	26	26	[111]
45	$H_2O_2 \cdot CO(NH_2)_2$ 230		$(MeCO)_2O$ 230  100	25	3			78	[62]
46[7,8]	30 % H_2O_2 160	$WO_3 \cdot H_2O$ 2.0	$Na_3PO_4 \cdot 12H_2O$ 1.3 $(C_8H_{17})_3N^+Me\ HSO_4^-$ 1.0 Gas − N_2	70 70	4 96			80 97	[112]
47[7]	 + H_2O_2 100		1 M NaOH 200	25	24			45	[113]
48	30 % H_2O_2 1300		$KHCO_3$ 200 DCC 200	25				83	[67]

TABLE 3 (Continued)

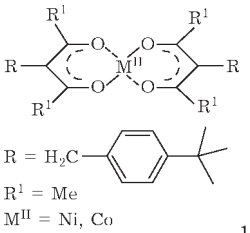
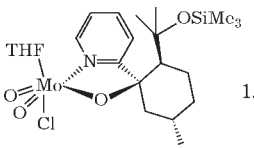
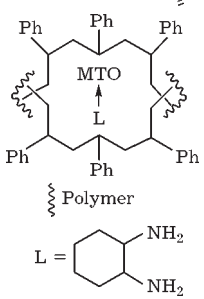
1	2	3	4	5	6	7	8	9	10
49	O_2	Co, $CoCl_2$, CrO_3, Cu complexes with pyridine, benzpyridine, picoline 1.0		65–90	4		54		[31]
50	O_2	 1.0	Me_2CHCHO 300	25	4	93	92	86	[41]
51	O_2	Alumophosphates AlPO-5 and AlPO-36 with substituting a part of Al by Mn or Co 0.97 mg per 1 mmol of olefin	Benzaldehyde 300	50	8	59	91	54	[114]
52	*t*-BuOOH 150	 1.0		55	24	63	13	8	[115]
53	35 % H_2O_2 150	 1.0		−10	1	>98	~100	98	[37]
54	O_2	Co on mesoporous SiO_2 7.1 mg per 1 mmol of olefin	MeCN	60	24	3	18	0.5	[74]
55	H_2O_2 300	Ti-SBA (65) – 573 mesoporous SiO_2 (SBA-15) grafted with Ti 10 mg per 1 mmol of olefin		70	24	~32	~100	35	[116, 117]

TABLE 3 (Continued)

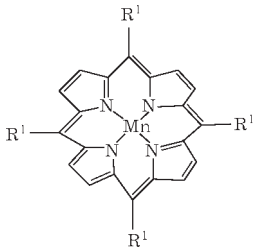
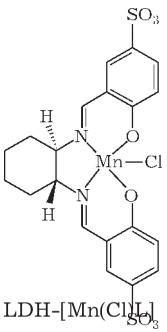
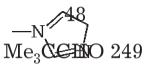
1	2	3	4	5	6	7	8	9	10
56[10]	*t*-BuOOH 160	Same as above, 14.3 mg per 1 mmol of olefin		80	24	91	100	91	[116, 117]
57	H_2O_2 100	 built-in to zeolite Y, 20 mg per 1 mmol of olefin	$MeCOONH_4$ 13	25	24	52	71	37	[47]
58[11]	O_2	 LDH-[Mn(Cl)L] Within the laminar solid such as hydrotalcite, the content of Mn being of 0.85 %, 27 mg per 1 mmol of olefin	 249	25	6	100	93	93	[8]

TABLE 3 (Continued)

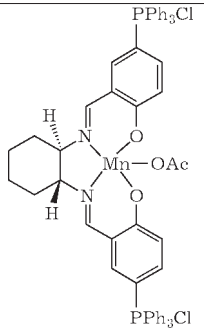
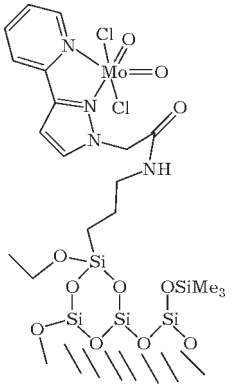
1	2	3	4	5	6	7	8	9	10
59	$NaIO_4$ 200	 on macroporous cationite Dowex MSCl, Mn(salen)Dowex 3.8		25	0.6	89	93	83	[58]
60	O_2	$Co(NO_3)_2$ 2.0	Me_2CHCHO 760	24	5.5	99	97	96	[42]
61	*t*-BuOOH 150	 Catalyst immobilized onto mesoporous modified substrate MCM-41 1.0		55		30–40	27	9.5	[118]
62	Anhydrous H_2O_2 200	Al_2O_3 neutral, pH 7		90	4	70	85	60	[39]

TABLE 3 (Continued)

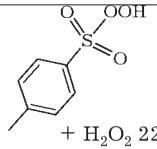
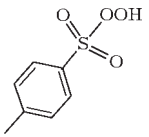
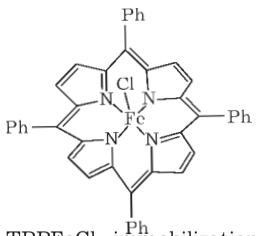
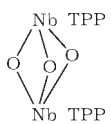
1	2	3	4	5	6	7	8	9	10
63[7]	 + H_2O_2 220		2 M NaOH up to pH 7.0–8.5	5–10	2–3	95	83	79	[68]
64[12]									[119]
65[7]	 + H_2O_2 150		2 M NaOH 150	25	1.5	~100	~70	~70	[120]
66	C_6H_5IO	 TPPFeCl, immobilization onto dextrin 0.2 is possible		25	8			91–92	[50]
67	NO_3 radical in an inert gas flow			25				~60	[121]
68	100 % H_2O_2 200	$CF_3(CF_2)_8CO(CF_2)_6CF_3$ 5.0	Na_2HPO_4 Gas – N_2	83	0.5			55	[122]
69[12]	MeCOOOH								[123]
70[13]	O_2	 TPP is tetraphenyl-porphyrinato 0.01	Irradiation by a mercury-discharge lamp	25	8			~30	[124]

TABLE 3 (Continued)

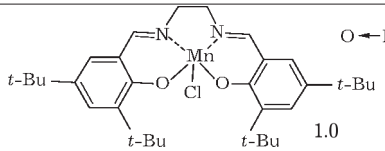
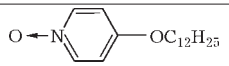
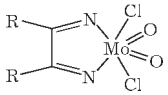
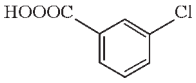
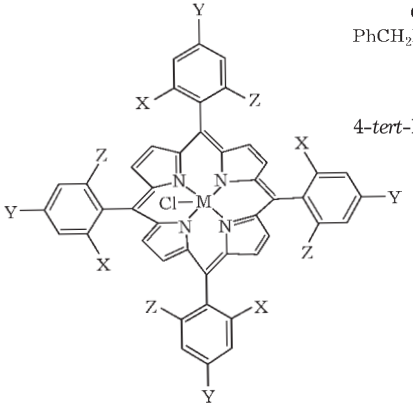
1	2	3	4	5	6	7	8	9	10
71	NaClO	 1.0		0	6			19	[125]
72	*t*-BuOOH 150	 immobilized onto mesoporous MCM-41, MCM-48, 24 mg per 1 mmol of olefin		55	24	~25	15	4	[126]
73	30 % H_2O_2	$MnSO_4$	$NaHCO_3$	25	52			~79	[127]
74			$NaHCO_3$					~90	[128]
75	Na_2CO_4		$(MeCO)_2O$, QAS, US						[129]
76	30 % H_2O_2		DCC 20, $KHCO_3$ 20	25	24			83	[130]
77	NaOCl 110	 X = NO_2, Y = Z = H, Mn(TNPP)Cl 0.5	Cl^- $PhCH_2N^+Me_2$ $C_{14}H_{29}$ 1.5 4-*tert*-Bu-pyridine 1.5	25		100	88	88	[131]

TABLE 3 (Continued)

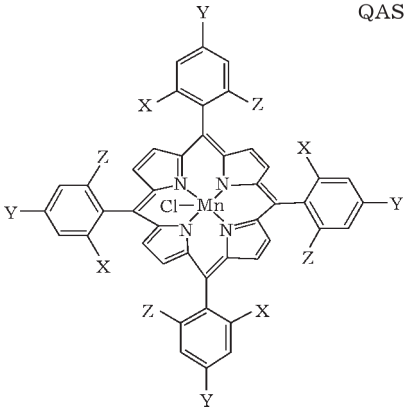
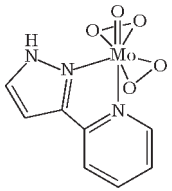
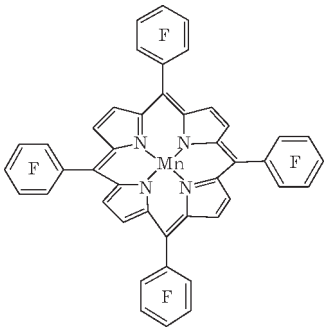
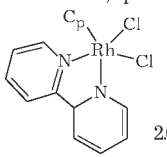
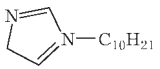
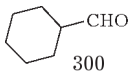
1	2	3	4	5	6	7	8	9	10
78	$KHSO_5$ 175	 Mn(TDCPP)Cl X = Z = Cl, Y = H 0.5	QAS 1.5	25		100	96	96	[132]
79	*t*-BuOOH	 0.17		100	1			24	[133]
80	O_2	 $MnTF_5PP$ 0.03	HCOONa, pH 8  2.0 Cp=$\eta^5C_5Me_5$ $(PhCO)_2O$ 100  3.3	40					[134]
81	O_2	$Cu(OH)_2$ 2.0	 300	25	17	100	83	83	[135]

TABLE 3 (Continued)

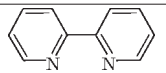
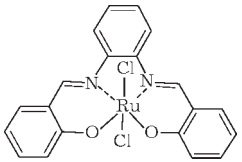
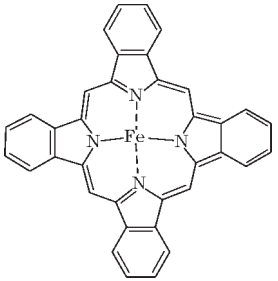
1	2	3	4	5	6	7	8	9	10
82	10 % H_2O_2 2500	MTO 1.0	 6.0	25 25	2 1	70 55	50 99	35 54	[136]
83[14]	O_2	 Incapsulated into zeolite Y 1.4 mg per 1 mmol of olefin		100	3	70	~35	24	[137]
84	O_2	$Co_4(\mu_3\text{-}O)_4 \cdot (\mu\text{-}PhCO_2)_4 \cdot (4\text{-}CNpy)_4$ complex with cubic structure 0.32		100	24	67	~65	44	[138]
85	*t*-BuOOH	$CpMoO_2Cl$, obtained *in situ* from $CpMo(CO)_3Cl$ and *t*-BuOOH 2.0		55	6	42	20	85	[139]
86	*t*-BuOOH	$Mo(CO)_5$, immobilized onto polystyrene through imidazole spacer, 40 mg per 1 mmol of olefin		76	9	100	100	100	[140]
87	Air	 Phtalocyanine complex 0.7		25	8			~26	[141]
88	*t*-BuOOH	$Mo(CO)_5$, immobilized onto polystyrene through piperazine spacer 1.1		76	3	97	100	97	[142]
89	O_2	Mn phtalocyanine complex	Me_2CHCHO						[143]

TABLE 3 (Continued)

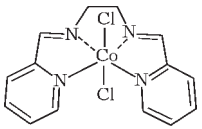
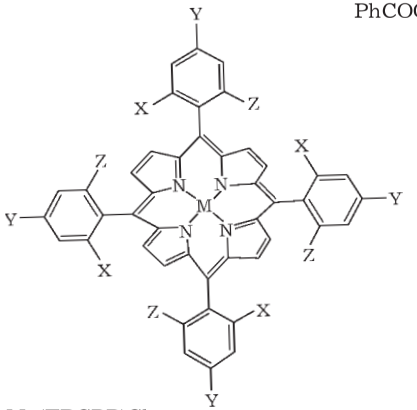
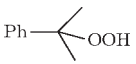
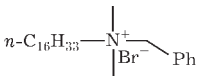
1	2	3	4	5	6	7	8	9	10
90	H_2O_2	Silanized high-disperse MCM-41 and MCM-48 with enhanced catalytic activity of Nb and Ta immobilized thereon							[144]
91	O_2	 5.0	Me_2CHCHO 200	25	10–15			70	[29]
92	30 % H_2O_2 200	 Mn(TDCPP)Cl X = Z = Cl, Y = H 0.5	PhCOOH 0.5	0	0.2	98	74	73	[145]
93	60 % H_2O_2 250	$(H_4N)_6Mo_7O_{24}^{-}$ –$(Bu_3Sn)_2O$		25	3	59	97	57	[146]
94	*t*-BuOOH 	Oxomolybdenum incorporated into cationite				81 71			[25]
95	NaOCl	Mn^{3+}-tetraphenylporphyrin containing MeCOO group	Pyridine, 					53	[147]

TABLE 3 (Continued)

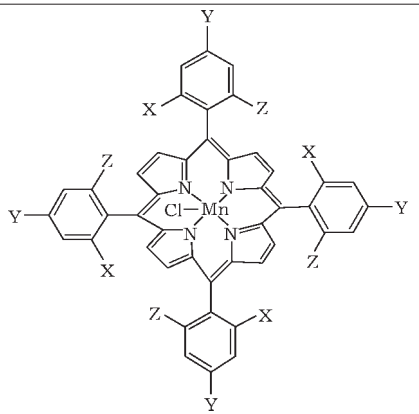
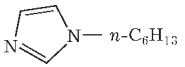
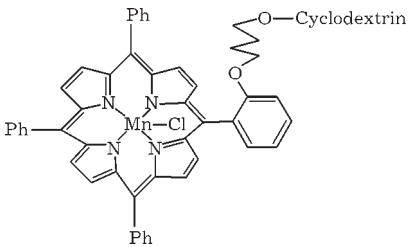
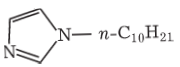
1	2	3	4	5	6	7	8	9	10
96	30 % H_2O_2 200	 Mn(TDCPP)Cl X = Z = Cl, Y = H 0.5	 0.5 PhCOOH 2.0	0	0.2	98	74	73	[148]
97	30 % MeCOOOH		Na_2CO_3	30−35	1.5−2			96	[149]
98[15,16]	O_2		 Light with λ > 350 nm	25	8			~50	[150]
99	$CO(NH_2)_2 \cdot H_2O_2$				3			78	[62]
100	Air	Mn^{3+}(TPP) $+Rh^{3+}(\eta^5\text{-}C_5Me_5)(bipy)Cl_2$ 1.75	 3.5 $(C_6H_5O)_2O$ 17 540 HCOONa 35 Et_3N up to pH 8.5	40	1			~53	[151]

TABLE 3 (Continued)

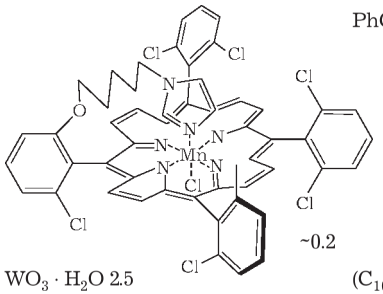
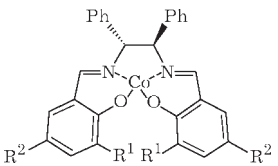
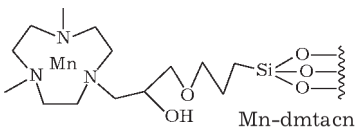
1	2	3	4	5	6	7	8	9	10
101	10 % H_2O_2 200	MTO 1.0		20	1	55	98	54	[109]
102	Air	Mn^{3+}(TPP) with 1-methylimidazole as an axial ligand	HCOONa	40	8	Epoxide content in the product is equal to 100 %			[152]
103[17]	30 % H_2O_2	 ~0.2	PhCOONa up to pH 4.5	0	1.3	95	92	87	[46]
104[18]	30 % H_2O_2	$WO_3 \cdot H_2O$ 2.5 or MoO_3, or H_2WO_4	$(C_{10}H_{22})_3N$ 3.0 $Na_3PO_4 \cdot 12H_2O$ 1.6 Gas – N_2	60	3			89	[153]
105[19]	O_2	 Catalyst is incorporated into macroporous zeolite, Co total content is 0.29 %, $R^1 = R^2 = t$-Bu, 13.5 mg per 1 mmol of olefin	Me_3CCHO	25	3	100	96	96	[59]
106	O_2	$CoCl_2$ 0.5–1.0		60	4	48–55	30	15	[154]
107	H_2O_2 220	 Mn-dmtacn		0	20	26	46	12	[60]

TABLE 3 (Continued)

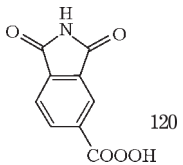
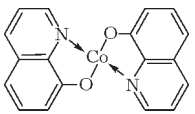
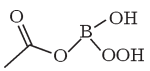
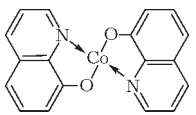
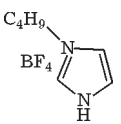
1	2	3	4	5	6	7	8	9	10
108	*t*-BuOOH 150	SiO_2 containing Mo in the form of isopropionate Mo(O-*i*-Pr)-SiO_2	Cyclohexane $(C_4H_9)_2O$ 25	80 80	8 24	32 44	41 34	13 15	[155]
109	 120			20	2			98–100	[156]
110	O_2 в MeCN	 on conjugated N-containing polymers	Me_2CHCHO	60				20–80	[157]
111	Air 1 MPa	Nanosized TiO_2		70		35	41	14	[158]
112	MeCOOOH								[159]
113	Air	Mn and Fe complexes with tetraphenylporohyrin							[51]
114[20]	 107	MnAlPO-5 9.3 mg per 1 mmol of olefin	H_2O 4218 pH 5.2	65 65	1 4	78 89	100 69	78 61	[160,161]
115	O_2 в MeCN	 on conjugated N-containing polymers	Me_2CHCHO 200	65	1			59	[162]
116[21]	H_2O_2 *in situ*	$MnSO_4$	CO_2, O_2, ionic liquid 	5–20	3–5	75	83	62	[70]

TABLE 3 (Continued)

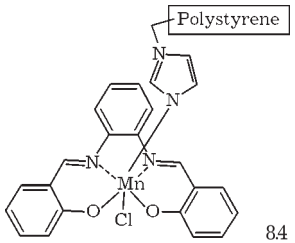
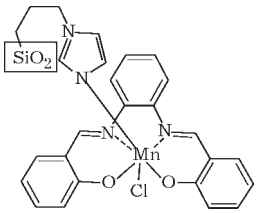
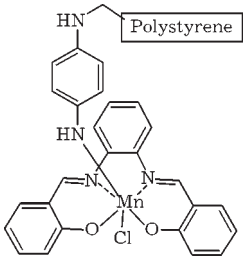
1	2	3	4	5	6	7	8	9	10
117	$NaIO_4$ in aqueous medium 200	 8.4		25	2.5	100	92	92	[163]
118	Air, 3 MPa	$Mn_{0.04}Al_{0.96}PO_4$-36 0.97 mg per 1 mmol of olefin	Benzaldehyde 300	50	8	59	91	54	[161]
119	$NaIO_4$ in aqueous medium 200	 8.4		25	3	100	90	90	[164]
120	$NaIO_4$ in aqueous medium 200	 10.8		25	2.5	93	94.6	88	[165]
121[22]	H_2O_2 *in situ*	$MnSO_4$ 0.06 mol. %	Anolyte – 2 M H_2SO_4, Catholyte – 1 M $NaHCO_3$, *tert*-butanol, O_2	25	1.5			23	[71]

TABLE 3 (Continued)

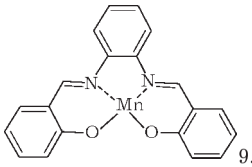
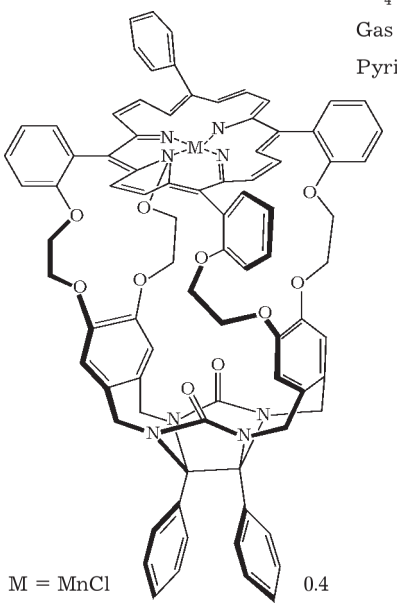
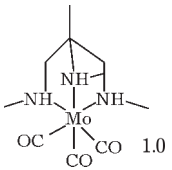
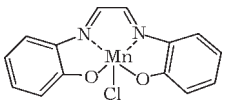
1	2	3	4	5	6	7	8	9	10
122	MeCOOOH 30 % H_2O_2	 9.4	MeCOOH $NaHCO_3$ NaOH						[166]
123	$NaIO_4$ in aqueous medium 200	incapsulated in zeolite Y with nanopores		25	10	92	93	86	[167]
124	NaClO in aqueous medium 100	 M = MnCl 0.4	Bu_4NCl 0.8 Gas − N_2 Pyridine 0.4	25	3			81	[45]

TABLE 3 (End)

1	2	3	4	5	6	7	8	9	10
125	*t*-BuOOH (5.5 M in decane) 154	 1.0		55	24	12	54	6.5	[168]
126	O_2	$[Bu_4N]_4H[PW_{11}Co(H_2O)O_{39}]$ on mesoporous silicate matrices 0.6	Me_2CHCHO 400	25	2.0	96	94	90	[43]
127[23]	Anhydrous 24 % H_2O_2 (sol. in ethyl acetate) 200	Al_2O_3, 5 mg per 1 mmol of terpene		77	6	32	62	20	[38]
128	O_2		Me_2CHCHO 500	35	6	70	47	33	[169]

[1] An activity series for Co, Fe, Mn, Ni acetyalcetonates is presented; electron donating substituents in acetylacetonates raise the activity of the catalyst.

[2] An ionic liquid was used as a solvent which can be used repeatedly.

[3] Chiral epoxide with *ee* up to 58 % is formed with the use of chiral Mn complex.

[4] The reaction mixture contained 46 % of verbenone and 21 % of epoxide.

[5] Data concerning the epoxidation of dodecene-1.

[6] An alternative catalyst is the complex twinned through oxygen.

[7] An epoxidizing agent is formed *in situ*.

[8] Data concerning the epoxidation of 3-carene.

[9] Epoxidation with distilling water out of the reaction mixture.

[10] Etching of the catalyst is observed.

[11] Epoxide with enantiomeric excess of 98 % is formed due to chiral ligand.

[12] There are no specific data in the abstract concerning the experiment.

[13] An alternative catalyst is O=MoTPP(OMe).

[14] Co can be used instead of Ru.

[15] Iron complex could be used, too.

[16] Epoxide obtained contains an excess of S-isomer up to 67 %.

[17] The structure of catalyst can vary with respect to substituents in the benzene rings, regarding axial ligands, regarding bonds between the aryl groups.

[18] Data concerning the epoxidation of cyclooctene.

[19] Epoxide obtained contains an excess of S isomer up to 91 %.

[20] Solid epoxidizing agent such as acetylperoxyborate on MnAlPO-5 reacts with water to produce acetic acid and hydrogen peroxide.

[21] Hydrogen peroxide is formed from the alkaline solution of ionic liquid containing oxygen.

[22] Hydrogen peroxide is formed from $NaHCO_s$, solution containing oxygen.

[23] Aluminium oxide obtained *via* sol-gel method and calcinated at 400 °C was used.

Notes. 1. Numbers in the formulas of epoxidizing agents, catalysts, auxiliary reagents designate the dosage of these compounds in mol % with respect to terpene except as otherwise noted. 2. The results epoxidation are characterized by the conversion level for terpene, selectivity with respect to epoxide and the yield of epoxide; if one of the three parameters is not specified in the reference, it was calculated according to under the formula: selectivity = yield/conversion level [78]. 3. From several results obtained in the same work under close conditions, the Table demonstrates the best one. 4. Some notes are caused by the fact that there is sometimes no example in a patent for the epoxidation of terpene which the Table is devoted to; in this case the Table displays the epoxidation parameters for another terpene presented in this patent.

TABLE 4

Main conditions and results for limonene epoxidation

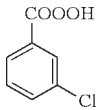
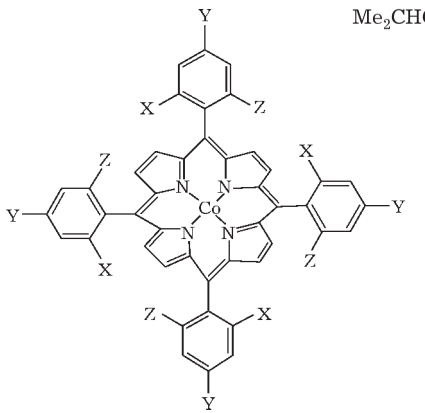
No.	Epoxidizing agent	Catalyst	Auxiliary reagents, co-catalysts	T, °C	Reaction time, h	Conversion level, %	Selectivity, %	Yield, %	Ref.
1	2	3	4	5	6	7	8	9	10
1	$H_2O_2 \cdot CO(NH_2)_2$ 300	$CF_3CH(OH)CF_3$ 1410		25	7	100	88	88	[170]
2	 100 or 230			25	12			82 or >90	[171]
3[1]	$F_2 + H_2O + MeCN$		$NaHCO_3$	−10	0.02			35	[172]
			Gas − N_2	0				35	
4	H_2O_2			50	4				[173]
5	*t*-BuOOH 160	Ti-SBA (65)-573 mesoporous SiO_2 SBA-15 grafted with Ti		80	24	97	100	97	[117]
6	O_2	$Ni(acac)_2$	Me_2CHCHO 300	25	2.5	100	81	81	[26]
7	O_2	 X = Z = H, Y = OMe Co(II)TPP-OMe 5.0	Me_2CHCHO 200	25	3			100	[52]

TABLE 4 (Continued)

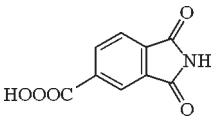
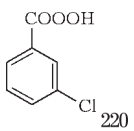
1	2	3	4	5	6	7	8	9	10
8	O_2	Co^{2+} complex with [3.2.1]cryptand and picrate [Co(L)](picrate)$_2$ 5.0	Me_2CHCHO 200	25	12–14			~100	[174]
9[2]	 100 or 200			20 20	2 2 + 4			~100	[156]
10	30 % H_2O_2 150		PhCN 150 $KHCO_3$ 100	25	48			86	[82]
11	*t*-BuOOH 100	MoO_3-4SiO_2 0.1 (molybdosilicate)		50	12	~85	~100	~85	[23]
12	30 % H_2O_2 150	MTO 0.5	Pyridine 12	25	11	96	98	94	[175]
13	50 % H_2O_2 200	Amberlite IRA-900 in the form of Venturello anion $PW_4O_{24}^{3-}$		38	24	84	93	78	[80]
14	MeCOOOH								[176]
15	60 % H_2O_2 200	$As(C_4H_9)_2Ph$ 1.0	Na_2HPO_4 5.0 Gas – N_2	~100	1.5			79	[177]
16	See Table 3, line No. 107					58	81	47	[60]
17	See Table 3, line No. 108					65 81	89 86	58 70	[155]
18	 220			~10	14			86	[178]

TABLE 4 (Continued)

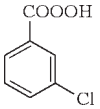
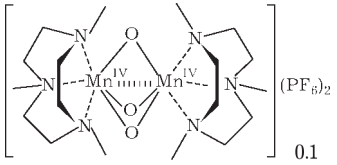
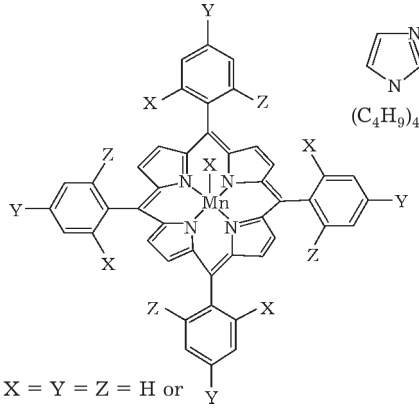
1	2	3	4	5	6	7	8	9	10
19[3]	 200 or 100		Gas − Ar	−5 0	4 1	87 100	~100 ~100	100 100	[110]
20	 220			0−20	~12				[179]
21[4]	See Table 3, line No. 40							83	[28]
22	See Table 3, line No. 91							54	[29, 180]
23	30 % H_2O_2 500	 0.1	MeCOOH 100	25	0.25	59	81	48	[108]
24[5]	See Table 3, line No. 39			25 25	1.5 8	90−100 90−100	91 37		[27]
25	30 % H_2O_2 200	$Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ (hydrocalcite) 0.94	Ultrasound	70	3			61	[181]
26	$NaIO_4$ 200	 X = Y = Z = H or X = Y = Z = Me X = AcOO	 12 $(C_4H_9)_4NBr$ 12	24 24	3 3.5	98−100 83	 95	88 79	[182]

TABLE 4 (Continued)

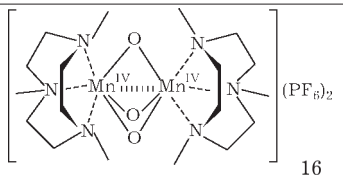
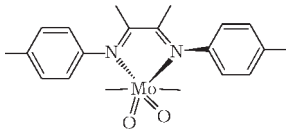
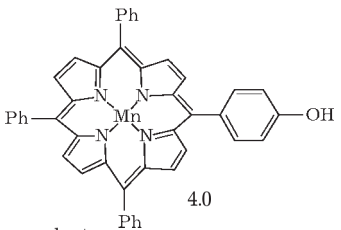
1	2	3	4	5	6	7	8	9	10
27[6]	30 % H_2O_2 500	 16	MeCOOH 100	25	0.25	59	81	48	[22]
28	*t*-BuOOH 150			55	4	82	95	78	[183]
29	30 % H_2O_2 400	$Ca_{10}(PO_4)_6(OH)_2$ (hydrocalcite) 8 mg per 1 mmol of olefin		65–70	8			38	[184]
30	$NaIO_4$ 200	 4.0 on polystyrene	 43	25	24			68	[185]
31		See Table 4, line No. 23		25	1			72	[32]
32	35 % H_2O_2 30	Ti-containing MCM-41 1.27 % Ti 9.3 mg per 1 mmol of olefin		70	7		50–60		[186]
33	30 % H_2O_2	$(n\text{-}Bu_4N)_2HP_2W_2O_{14}$, fixed onto resin Amberlyst or onto porous SiO_2		20	4	100	95	95	[187]

TABLE 4 (Continued)

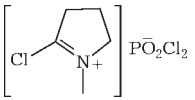
1	2	3	4	5	6	7	8	9	10
34	30 % H_2O_2 4100		 250 18-crown-6 4.0 Gas – N_2	−20...+20	2	78	85	66	[188]
35[7]	30 % H_2O_2 100	$[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$ × × $[(n\text{-}C_4H_9)_4N^+]_4$ polyoxovanadometallate TBA-1 5.0		20	24			89	[33]
36	O_2	Hydrotalcite containing Mg, Al, Cu, Pd		80	6	55			[189]
37		See Table 3, line No. 59				85	100	85	[58]
38	$NaIO_4$	Mn(TPyP) fixed onto chloromethylated polystyrene	Ultrasound						[190]
39		See Table 3, line No. 56				97	100	97	[116, 117]
40	35 % H_2O_2 200	$K_{5.5}Na_{1.5}[PW_{10}O_{38}Cu_4(H_2O)_2] \cdot 13H_2O$, main phase $[K_{10}(PW_9O_{34})_2Cu_4(H_2O)_2] \cdot 20H_2O$, minor phase 0.1		2	40				[191]
41	35 % H_2O_2 130	MTO	Pyridine 20 or 3-cyanopyridine 20	20	6			~90	[1]
42		See Table 3, line No. 44				92	82	75	[111]
43		See Table 3, line No. 45						95	[62]
44	60 % H_2O_2 200		Na_2HPO_4 5.0 Gas – N_2	~80	3			81	[24]
45		See Table 3, line No. 48						85	[67]
46		See Table 3, line No. 19				17	26	4.5	[73]

TABLE 4 (Continued)

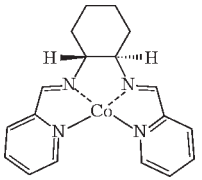
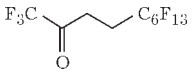
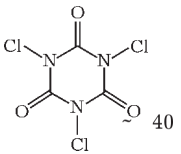
1	2	3	4	5	6	7	8	9	10
47[8]	O_2	 in mesopores of zeolite X 13.5 mg per 1 mmol of olefin	Me_3CCHO 311 N-methylimidazole 51	25	24		81		[192]
48[9]	O_2	Co-salen with a chiral ligand in mesoporous zeolite	Me_3CCHO N-methylimidazole						[193]
49[10]		See Table 3, line No. 52				90	71 for $R(+)$ 83 for $S(-)$	64 75	[115]
50	OKCOH		$NaHCO_3$ 600 EDTA ~0.06	25	4.5	90	79	71	[194]
51[11]	HClO from TCICA		 40 KOH ~110	25				45	[195]
52		See Table 3, line No. 57				21	100	21	[47]
53		See Table 3, line No. 54		60	24		30		[74]
54		See Table 3, line No. 59				85	100	85	[58]
55[12]		See Table 3, line No. 58				95	93	88	[8]
56		See Table 3, line No. 62				70	90	63	[39]
57									[196]
58	Anhydrous H_2O_2 200	Al_2O_3 neutral obtained using sol-gel method		76	9	~95			[197]
59		See Table 3, line No. 106				43	43	18.5	[154]

TABLE 4 (Continued)

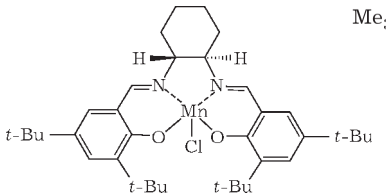
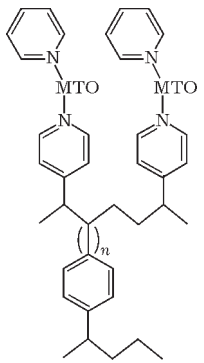
1	2	3	4	5	6	7	8	9	10
60	O_2	 136 mg per 1 mmol of olefin	Me_3CCHO 2.5	25	24	90–95	55–60	~52	[59]
61[13]		See Table 3, line No. 61				50–55	97	51	[118]
62	PhIO	Mn(III)salenCl 1.0	Gas – N_2 or Ar	25	25		47	26	[57]
63	$H_2O_2 \cdot CO(NH_2)_2$ 220	MTO		20	0.4	52			[198]
				20	0.7	99			
64	35 % H_2O_2 120	 MTO in polyvinylpypridine with 25 % linkage		25	1.5	79			[36]
65		See Table 3, line No. 42		20	0.5	>99	98	97	[109]
66		See Table 3, line No. 82		4	1	92	93	85.5	[105, 136]
				4	2	98	86	84	
67		See Table 3, line No. 93				82			[25]

TABLE 4 (Continued)

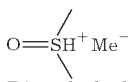
1	2	3	4	5	6	7	8	9	10
68[11]		See Table 3, line No. 47							[113]
69		See Table 3, line No. 50				77	93.5	72	[41]
70[14]		See Table 3, line No. 85				100	20	20	[139]
71		See Table 3, line No. 68						72	[122]
72[15]		See Table 3, line No. 21				93–99		61–74	[94]
73		See Table 3, line No. 76						85	[130]
74		See Table 3, line No. 54			2–2.5	96–98	~100	98	[37]
75		See Table 3, line No. 29						72	[22]
76[16]		See Table 3, line No. 58				95	93	88	[131]
77		See Table 3, line No. 79						100	[133]
78	50 % H_2O_2 150		Phenol MeCOONa 1.0	40	22	86	92	79	[199]
79	O_2	Pr compound, 1 mass %	$MeCH_2CHO$ 150	30–60	4.5	94	81	76	[84]
80		See Table 3, line No. 110							[157]
81	30 % NaOCl в H_2O *t*-BuOOH 100	Complexes of Fe, Mn, Co with tetraphenylporphyrine (FeTPP)Cl, (MnTPP)Cl, CoTPP 0.1		30	4	80			[200]
82	 Dimethylsulphonium methylide								[201]
83		See Table 3, line No. 114				94	61	57	[160, 161]
84		See Table 3, line No. 115			2			86	[162]
85		See Table 3, line No. 117				92	71	65	[163]
86		See Table 3, line No. 119				92	98	90	[164]
87		See Table 3, line No. 123				89	100	89	[167]

TABLE 4 (Continued)

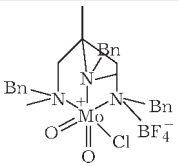
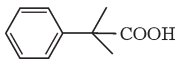
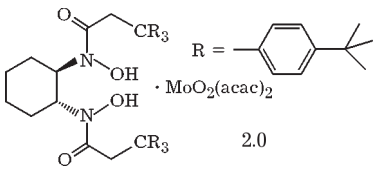
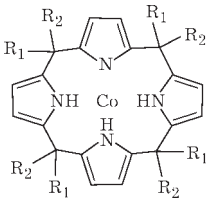
1	2	3	4	5	6	7	8	9	10
88	*t*-BuOOH (5.5 M in decane) 154	 1.0 Bn = $C_6H_5CH_2$		55	24	34	84	28.5	[168]
89		See Table 3, line No. 127				40	80	32	[38]
90		See Table 3, line No. 120				95	100	95	[165]
91[17]	 150	 2.0		25	46			94	[202]
92	H_2O_2	$[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$ polyoxometallate							[203]
93		Halogenation of limonene by means of N-bromosuccinimide with further treatment of bromohydrines formed by the mixture of Na_2CO_3 – EtOH – H_2O yields *trans*-1,2-epoxylimonene						54	[204]
94[18]	30 % H_2O_2 100	$[\gamma\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$ $(Bu_4N^+)_4$ 5.0		20	24	95	95	90	[65, 66]
95[19]	O_2	 R_1 = Me, R_2 = 4-methoxyphenyl, Co(II)calyx(4)pyrrol 1.0	Et_2CHCHO 200	30	24			82 93	[205]

TABLE 4 (Continued)

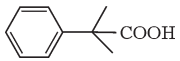
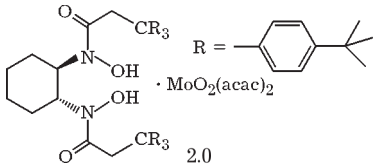
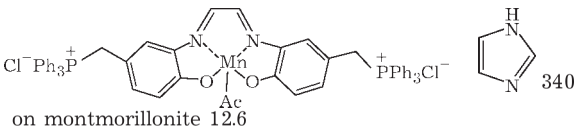
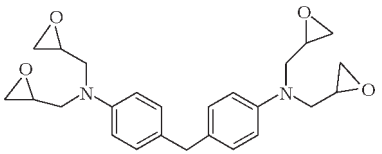
1	2	3	4	5	6	7	8	9	10
96[20]	*t*-BuOOH or  150	 2.0		25	46			47	[206]
97	Anhydrous H_2O_2 (р-р в ЭА) 200	Basic Al_2O_3 0.25		60	8	31	97	30	[40]
98[21]	*t*-BuOOH (5.5 M in decane) 150	Me_2-menthyl-$Sn_2MoO_4(H_2O)_{3.5}$ 1.0		55	24	85 97	89 68	76 66	[207]
99	O_2	Mn complex with meso-tetraphenylporphyrin (MnTPP)	Me_2CHCHO 500	25	5	92	99	91	[208]
100	*t*-BuOOH 110	Ti-MCM-41 (MCM-41 with grafted Ti (IV)) 0.002 % Ti			24	77	81	62	[209]
101		See Table 3, line No. 40						91	[210]
102	$NaIO_4$ in H_2O 200	 on montmorillonite 12.6	340	25	4	87	100	87	[211]
103	30 % H_2O_2 in phosphate buffer 150	$Na_2WO_4 \cdot 2H_2O$ 2.0	$(n\text{-}C_8H_{17})_3N^+Me$ (HSO_4^-) 1.0 0.1 M H_3PO_4 0.1 M NaH_2PO_4 Na_2SO_4 5.0	25–70	2.2	98	64	63	[212]
104	*t*-BuOOH (3.2 M in toluene) 120	 4,4'-methylene-bis(N,N-diglycidylaniline; TGMDA-Mo$(OEt)_5$ 50 mg per 1 mmol of terpene		90	24	86	90	77	[213]

TABLE 4 (Continued)

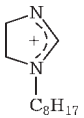
1	2	3	4	5	6	7	8	9	10
105	3 % *t*-BuOOH in acetone 800	V_2O_5/TiO_2, 3.4 mg per 1 mmol of terpene		60		16	23	3.7	[214]
106	H_2O_2 316	$[AsO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2][(n\text{-}C_6H_{13})_4N]_3$	Phase transfer catalyst Gas – N_2	25	6	98	88	86	[215]
107		Detailed investigation of epoxidation kinetics under the action of H_2O_2 in the presence of PW-amberlite							[216]
108[22]	30 % H_2O_2 100	 $[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$, immobilized on SiO_2 using 0.005 % polyoxometallate as a binding agent		20	24			80	[217]
109	70 % *t*-BuOOH in H_2O 200	Mn complex withtetraphenyl-porphyrin and chlorine as an axial ligand Mn(TPP)Cl 0.1		30	4	80			[55]

TABLE 4 (Continued)

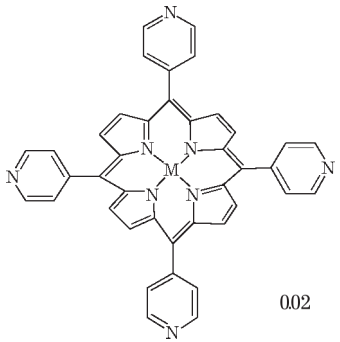
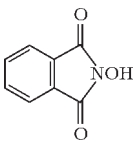
1	2	3	4	5	6	7	8	9	10
110	~4 % $NaIO_4$ in H_2O 200	 0.02 Tetra-(4-pyridyl)porphyrin immobilized onto chloro-methylated polystyrene	 20 Ultrasound	25	0.34	94	94	88	[48]
111	Air	 10	MeCHO 300	25	14			100	[218]
112	*t*-BuOOH (~6 M in decane)	MoO_x, incorporated into grinded SiO_2, 0.62 % Mo		25	24	94	93	87	[61]

TABLE 4 (Continued)

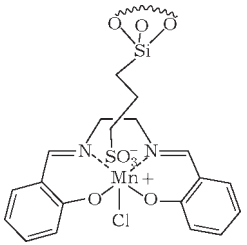
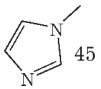
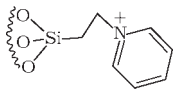
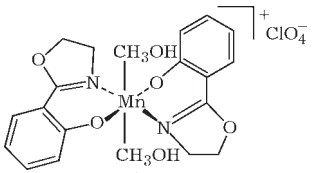
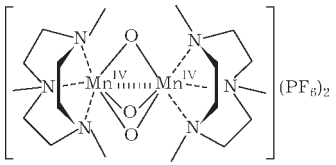
1	2	3	4	5	6	7	8	9	10
113	Air	 Mn(salen) immobilized onto zeolite SBA-15 modified with sulphuric acid (SBA-15-pr-Mn(salen)) 27 mg per 1 mmol of olefin	Me_2CHCHO 240  45	25	12	60	90	54	[219]
114	Anhydrous H_2O_2 in *t*-BuOH 428	 × $[HPO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}]^{2-}$ 8.5 W Polyoxometallate complex on modified SiO_2		22	22	86	81	70	[220]
115	35 % H_2O_2 200	$K_{5.5}Na_{1.5}[PW_{10}O_{38}Cu_2(H_2O)_2] \cdot 13H_2O$ 0.2		2	40		96		[221]
116		O_2 blow-through during 6 h at 80 °C through orange oil containing 0.1 % of Pd on hydrotalcite results in limonene conversion level of about 40 % with the selectivity at about 40 % with respect to epoxides							[222]
117	$(H_2N)_2CO \cdot H_2O_2$ 400	 Hphox = 2-(2′-hydroxyphenyl)oxazoline $Mn(phox)_2(CH_3OH)_2ClO_4$ 6.7	 133	25	0.08			75	[223]

TABLE 4 (End)

1	2	3	4	5	6	7	8	9	10
118	MeCOOOH 576	 Binuclear complex of Mn(IV) with 1,4,7-trimethyl-1,4,7-triazacyclononane (L) $[Mn_2L_2O_3](PF_6)_2$ 0.04		25	1.0	~80	~100	82	[224]
119[23]	30 % H_2O_2 134	$WO_3 \cdot H_2O/H_2O_2-H_2O-H_3O^+$ 1.7	$MeN^+(n\text{-}C_8H_{17})_3H_2PO_4^-$	21	2	95	58	55	[225]
120[24]	35 % H_2O_2 27	Ti-MCM-41 silanized with hexamethyldisilazane 11.6 mg per 1 mmol of olefin		70	7	81	65		[226]

[1]At an elevated temperature diepoxides are formed.

[2]An equimolar amount of the epoxidizing agent results in the formation of 1,2-monoepoxide, whereas double amount of the epoxidizing agent and triple exposition is stated (with no indication of quantitative parameters) to result in the formation of diepoxides.

[3]The ratio between mono- and diepoxides depends to a considerable extent on the conditions and the quality of source epoxide.

[4] Epoxidation with distilling water out of the reaction mixture.

[5] There is also a description of other modifications of the catalyst with the characteristics different from the presented.

[6] With varying the concentration of hydrogen peroxide from 100 to 30 % the content diepoxides decreases from 47 to 22 %.

[7] Only 8,9-epoxide is formed.

[8] The enantiomeric excess of epoxide is 37 %.

[9] The catalyst it is used for stereoselective oxidation.

[10] The selectivity for the epoxidation of *R*-(+)-isomer is 71 %, whereas for the epoxidation of *S*-(−)-isomer this value is equal to 83 %, which, probably, could be connected with different purity of the reagents.

[11] An epoxidizing agent is formed *in situ*.

[12] The diastereomeric excess for one of the isomers of the epoxide is equal to 43 %.

[13] For a non-silanized catalyst just the same result is obtained as for a silanized catalyst.

[14] An epoxidizing agent is formed *in situ* from $CpMo(CO)_3Cl$ and *t*-BuOOH.

[15] The result depends on metal and polymer used.

[16] Epoxide with the diastreomeric excess of 43 % is formed due to chiral ligand.

[17] The diastereomeric excess of epoxide is equal to 66 %.

[18] 99 % of the mixture of epoxides is presented by 8,9-isomer.

[19] For *R*-(+) isomer the yield is less, than for *S*-(−) isomer.

[20] The diastereomeric excess of epoxide is 33 %.

[21] Top line: the conversion level, selectivity, yield for *R*(+)-l-monene; bottom line: those values for *S*-(−)-limonene and the values of diastereomeric excess of epoxides 5-7

[22] 97.5 % of the mixture of epoxides is presented by 8,9-epoxylimonene.

[23] The conversion of olefin occurs in a two-phase catalytic system with the key role of WO_3.

[24] Epoxidation carried out in the excess of olefin to prevent titanium from washing away. Sililation keeps the selectivity with an increase in the conversion level.

TABLE 5

Main conditions and results for 3-carene epoxidation

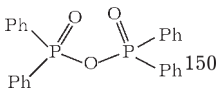
No.	Epoxidizing agent	Catalyst	Auxiliary reagents, co-catalysts	T, °C	Reaction time, h	Conversion level, %	Selectivity, %	Yield, %	Ref.
1	50 % H_2O_2, 100	 150	K_2CO_3 300	−5	12−0			80	[227]
2		See Table 3, line No. 46							[112]
3[1,2]		See Table 3, line No. 104							[153]
4[3]		See Table 3, line No. 40						87	[28]
5	30 % H_2O_2 160	$WO_3 \cdot H_2O$ 200	Na_3PO_4 3.0 QAS ~1.0 H_2SO_4 up to pH 2.5	25	96			97	[228]
6		See Table 3, line No. 53							[37]
7	50 % H_2O_2 150	$Zn(NO_3)_2 \cdot 6H_2O$ $+ Na_2WO_4 \cdot 2H_2O$ 630	$C_{20}H_{41}N^+(H_2PO_4^-)Me_2CH_2CH_2OH$ 440	60−65	85	~100	~78	78	[229]
8		See Table 3, line No. 42		20	2	97	99	96	[109]
9	50 % H_2O_2 250		MeCN 620 Na_2HPO_4 0.012 NaOH ~26 Gas − N_2	60	18			92	[230]
10	38.4 % MeCOOOH 110		Na_2CO_3 94 MeCOOOH NaOH ~26 Gas − N_2	20	24				[231]
11	50 % H_2O_2 250		MeCN 620 Na_2HPO_4 0.012 NaOH ~26 Gas − N_2	60	24				[231]

TABLE 5 (Continued)

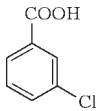
1	2	3	4	5	6	7	8	9	10
12	*t*-BuOOH	$(NH_4)_2MoO_4$ ~0.08	NaOH 500	97	6			~93	[231]
			Gas − N_2						
13		See Table 3, line No. 91						48	[29]
14		See Table 3, line No. 37		70	5				[107]
15	60 % H_2O_2 200		CF_3COCF_3 5.0	20	1			80	[232]
			Na_2HPO_4 5.0	20	21			>99	
16		See Table 3, line No. 49		25	22	70	25	17.5	[31]
				20	9	79	18	14	
17								80	[145]
18		See Table 3, line No. 7		20	5	97	90	87	[26]
19			Gas − Ar	−5	1			~100	[110]
20		See Table 3, line No. 39		20	1.5				[27]
21		See Table 3, line No. 3		60	4	97	97	94	[80]
22[4]	60 % H_2O_2 200		Na_2HPO_4 5.0,	20	21			81	[24]
			gas − N_2						
23[1]		See Table 3, line No. 63				62		~55	[68]
24	O_2	CoNaY	Me_2CHCHO 760	24	2.5	100	99	99	[42]
		$Co(NO_3)_2$ 2.0		24	3.0				
25	50 % H_2O_2 150	PhOH 1000	MeCOONa 1.0	60	12	96	95	91	[199]
26[5]	30 % H_2O_2 600−700	$(TBA)_6[Mn(H_2O)BW_{11}O_{39}]$ $(TBA)_5[BW_{12}O_{40}]$		82	2−6	75−76	62−65	44−47	[234]

TABLE 5 (Continued)

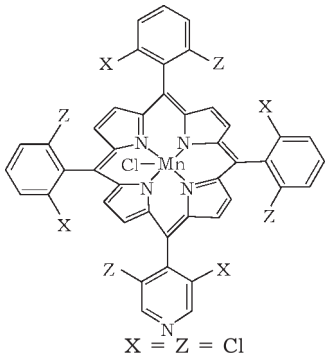
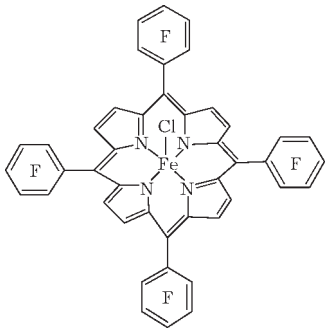
1	2	3	4	5	6	7	8	9	10
27	30 % H_2O_2 300	 X = Z = Cl $[MnClTDCPPyPH]H_2[PW_{12}O_{40}] \times$ $\times 4H_2O \cdot 3MeOH$	$MeCOONH_4$ 66	60	1.5	68	57	39	[235]
28	MeCOOOH		MeCOONa	25	2			98	[236]
29	30 % H_2O_2			23	24			93.5	[237]
30[1]		See Table 3, line No. 47						22	[113]
31	10 % H_2O_2 200	 Fe(TPFPP)Cl 0.2		22	1	98	92	90	[238]

TABLE 5 (Continued)

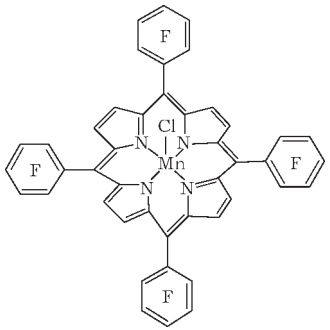
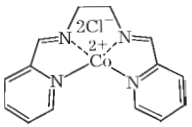
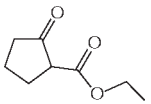
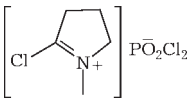
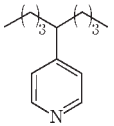
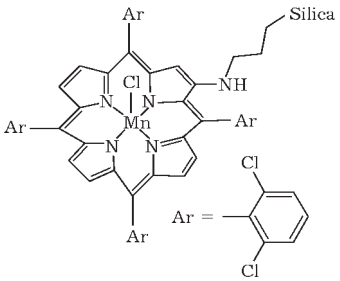
1	2	3	4	5	6	7	8	9	10
32	30 % H_2O_2 420	 Mn(TF$_5$PP)Cl 1.7	MeCOONH$_4$ 23	25	3.5	100	60	60	[239]
33	50 % H_2O_2 200	PW_4O_{24} on Amberlite IRA-900 20 mg per 1 mmol of terpene		38	24	55	97	53	[80]
34	O_2	Pr compound, 1 mass %	MeCH$_2$CHO 150	30–60	4	95	82	78	[84]
35	Anhydrous MeCN	 ~5.0		25	30			35	[180]
36[6]	30 % H_2O_2 4100		 150 8-crown-6 4.0 gas – N_2	−20	2			27	[188]
37[2]	30 % H_2O_2 530	$WO_3 \cdot H_2O$ 250 or MoO_2 240	 2.4 H_3PO_4 1.6	60	2			77 85	[240]

TABLE 5 (End)

1	2	3	4	5	6	7	8	9	10
38	30 % H_2O_2 in phosphate buffer	$Na_2WO_4 \cdot 2H_2O$ 2.0	$MeN^+(n\text{-}C_8H_{17})_3$ HSO_4^- 1.0 0.1 M H_3PO_4 0.1 M NaH_2PO_4 Na_2SO_4 5.0	25–70	4.0	93	95	88	[241]
39	35 % H_2O_2	 5,10,15,20-tetrakis(2,6-dichlorophenyl)-porphyrinato-Mn(III) [Mn(TDCPP)Cl] 103 mg per 1 mmol of olefin	$MeCOONH_4$ 40	20	27	65	42	27	[49]
40[7]	30 % H_2O_2 134	$WO_3 \cdot H_2O$/ H_2O_2–H_2O–H_3O^+ 1.7	$MeN^+(n\text{-}C_8H_{17})_3$ $H_2PO_4^-$ 2.5	21	3	85	100	85	[225]

[1] An epoxidizing agent is formed *in situ*.

[2] Quantitative data are presented for the epoxidation of cyclooctene.

[3] Epoxidation with distilling water out of the reaction mixture

[4] The yield is presented for purified epoxide in small-scale experiment.

[5] The reaction duration depends on the excess of hydrogen peroxide.

[6] 70 % of initial terpene remain non-reacted.

[7] The conversion of olefin occurs in a two-phase catalytic system with the key role of WO_3.

TABLE 6

Main conditions and results for β-pinene epoxidation

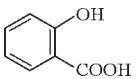
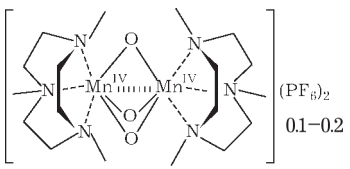
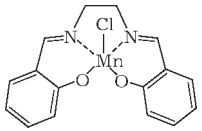
No.	Epoxidizing agent	Catalyst	Auxiliary reagents, co-catalysts	T, °C	Reaction time, h	Conversion level, %	Selectivity, %	Yield, %	Reference
1	2	3	4	5	6	7	8	9	10
1[1]		See Table 3, line No. 37							[107]
2		See Table 3, line No. 1						84	[79]
3	$(MeCOO)_4Pb$								[242]
4	PhCN + 50 % H_2O_2 ~1 : 1		$KHCO_3$ 49	20–25	120			74	[243]
5		See Table 3, line No. 5						91	[82]
6		See Table 3, line No. 2		0	1.2	98	83.5	82	[1]
7		See Table 3, line No. 4					84		[81]
8		See Table 3, line No. 109							[156]
9		See Table 3, line No. 104							[153]
10		See Table 3, line No. 48			24			91	[67]
11		See Table 3, line No. 50				27	85	23	[41]
12		See Table 3, line No. 94				72 69			[25]
13		See Table 3, line No. 95						49	[147]
14[1,2]		See Table 3, line No. 46		70	4			80	[112]
15	35 % H_2O_2 1000	$MnSO_4$ 2.0		20	3	97	78	76	[244]
16[3]		See Table 3, line No. 44				95	10.5	10	[111]
17[4]		See Table 3, line No. 63				90	52	47	[68]
18	Anhydrous H_2O_2 520		MeCOOH 100	25	0.25	14	70	10	[108,32]

TABLE 6 (End)

1	2	3	4	5	6	7	8	9	10
19[5]		See Table 3, line No. 76						91	[130]
20	PhIO 100	 5.0	Gas − N_2	25	4	55			[103]
21		See Table 3, line No. 82		0	5	60	90	54	[136]
22		See Table 3, line No. 8		30−60	5	83	48	40	[84]
23		See Table 3, line No. 128				96.7	63.9	62	[169]
24		Epoxidation of β-pinene at the 1st stage of the synthesis of perrylic aldehyde							[245]

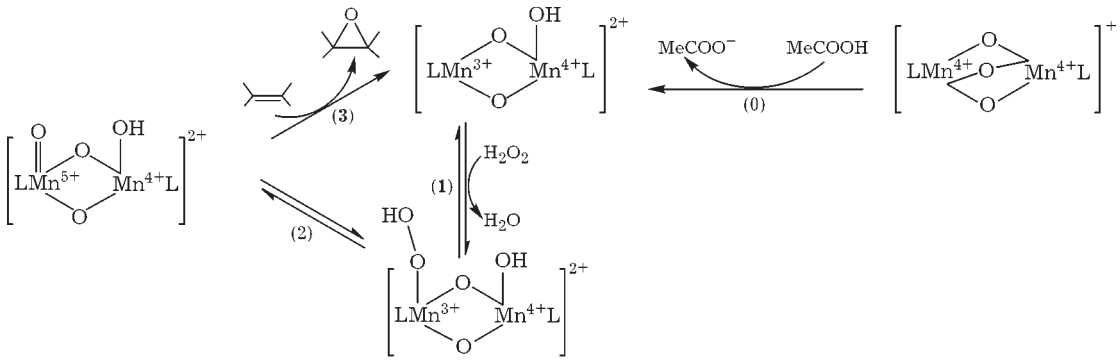
[1] Data concerning the epoxidation of 3-carene.

[2] An epoxidizing agent is formed *in situ*.

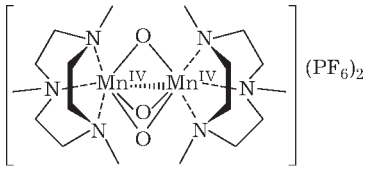
[3] The epoxidizing agent is air under a pressure of 3 MPa.

[4] The content of the main substance in the product is higher than 99 %.

[5] Methanol is used as a solvent instead of ethanol.



Scheme 4.



13

The complex **13** exhibits weak catalytic properties in the processes of oxidation-epoxidation. Nevertheless, the mechanism of epoxidation by this reagent has been studied in [22]. Scheme 4 demonstrates the stages of epoxidation, beginning from operation (0) – the formation of proper catalyst. It turns out that compound **13** represents only a precursor of the catalyst. The following conclusions are also drawn from the investigation [22]:

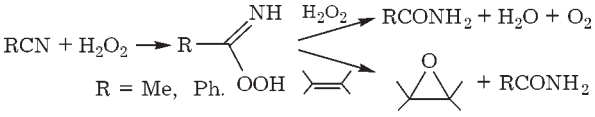
1. The most efficient method for using hydrogen peroxide in the epoxidation process consists in a batching entering of the reagent into the reaction medium.

2. Epoxidation proceeds according to the mechanism that, as against the process of alkanes oxidation by *t*-BuOOH, occurs without the formation of radicals.

3. Epoxidation is the first-order reaction with respect to the concentration of substance **13**.

4. The epoxidation of alkene and the parallel oxidation of alkane proceed through different intermediate species.

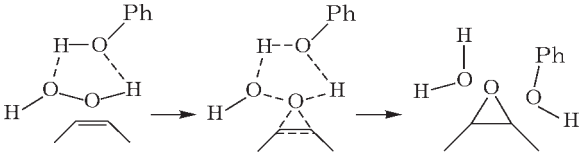
The most widespread solvent used in the reaction of epoxidation is acetonitrile which reacts with hydrogen peroxide to form peroxyacetimidic acid. The latter can transfer the oxygen to the double bond. PhCN operates in a similar manner [62, 63].



Thus, acetonitrile and PhCN could be considered to represent solvents, activators.

Some fluoroorganic solvents such as hexafluoropropanol-2, trifluoroethanol, hexafluoroacetone, fluorinated alkanes, amines, fluorinated ethers could be related to this kind of compounds, too. Such compounds are able to epoxidize terpenes either without additives, or with small amounts of nonmetallic additives (see Tables 3–6). The authors of these publications explain the "effect of fluorine" by physical features of fluorinated compounds, first of all by the ability to form associates and hydrogen bonds, which results in the stabilization of intermediate species responsible for the process of epoxidation as well as in the lowering of energy barriers of the reactions.

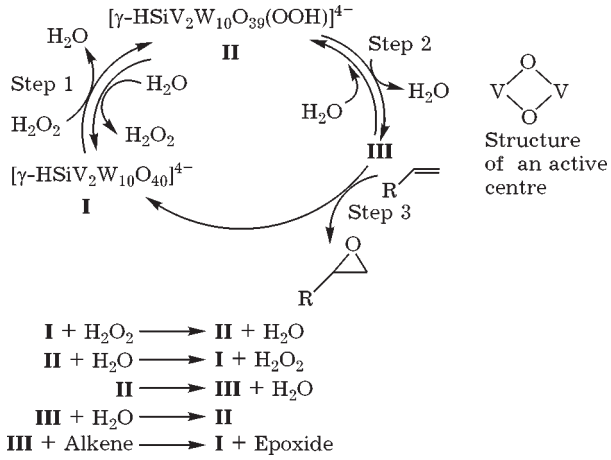
Phenol is proposed to be a solvent (activator), too [64]:



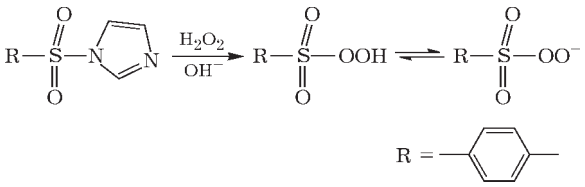
The ability of phenol molecules for aggregation, from the standpoint of the authors of [64] determines the stabilization of the transition state.

The increasing attention of researchers is attracted by such a group of catalysts as polyoxometallates. Their composition varies, but the permanent components of the anionic parts of

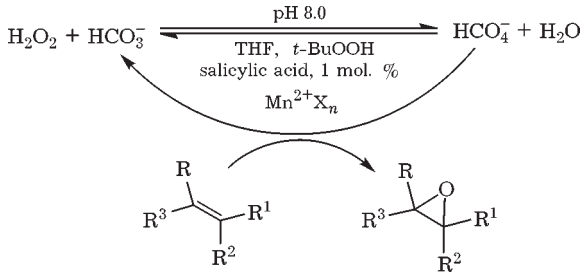
the molecule are presented by tungsten, silicon, hydrogen at a high content of oxygen. Tetabutylammonium cation is used as a counterion. It is established that polyoxometallates with the mentioned set of chemical elements can provide at 70 °C high yields of epoxides of various olefins already with a double excess of 15 % hydrogen peroxide solution. In case that the structure of polyoxometallate includes vanadium the diastereoselectivity, stereospecificity and regioselectivity become unique [65]. For example, in the process of limonene epoxidation by polyoxometallate $\{[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}\}$ containing no vanadium the content of 8,9-epoxide amounts to 37 % only. In the beginning of the studies on V-containing polyoxometallates their active nucleus was considered to represent $VO-(\mu\text{-}OH)_2-VO$ [33, 65]. The authors of the latest work described the structure of the active centre of the catalyst and have offered a cyclic mechanism for the epoxidation including five elementary processes [66].



Below one can see schematic diagrams for the interaction between the main epoxidizing agent such as hydrogen peroxide and special reagents (activators) those form in the reaction medium a more effective generators of the active oxygen, which active oxygen mainly causes the reaction to proceed (Scheme 5).



The activator is presented by arylsulphonylic peracid, a stronger epoxidizing agent as compared to perbenzoic acid [68].



The activators are manganese sulphate and salicylic acid [12]. The formation of HCO_4^- (peroxomonocarbonate) is proved using ^{13}C NMR technique [69].

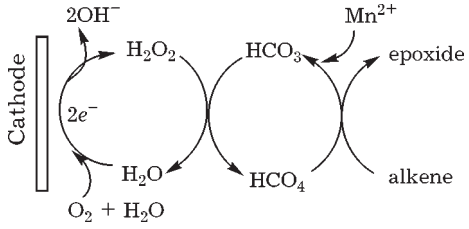
A group of Chinese authors has proposed a modification of this method whereby the epoxidation is carried out within the cathodic cell of an electrolyser generating hydrogen peroxide [70, 71]:

$$O_2 + e^- \rightarrow O_2^{\bullet -}$$

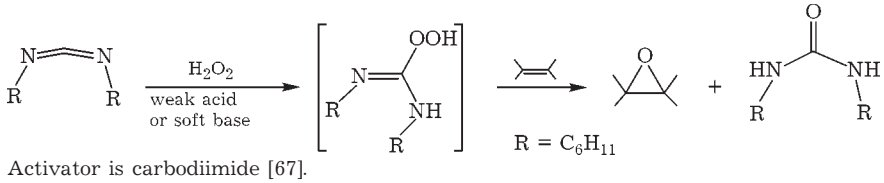
$$2O_2^{\bullet -} + 2H_2O \rightleftharpoons O_2 + H_2O_2 + 2OH^-$$

$$O_2 + 2H_2O + 2e^- \rightleftharpoons H_2O_2 + 2OH^-$$

Using different catholyte compositions whereto oxygen was fed the researchers epoxidized a number of compounds including α-pinene:



The authors consider the possibility of controllable dosing hydrogen peroxide fed into the reaction mixture to be the advantage of the method. Unfortunately, the data presented in

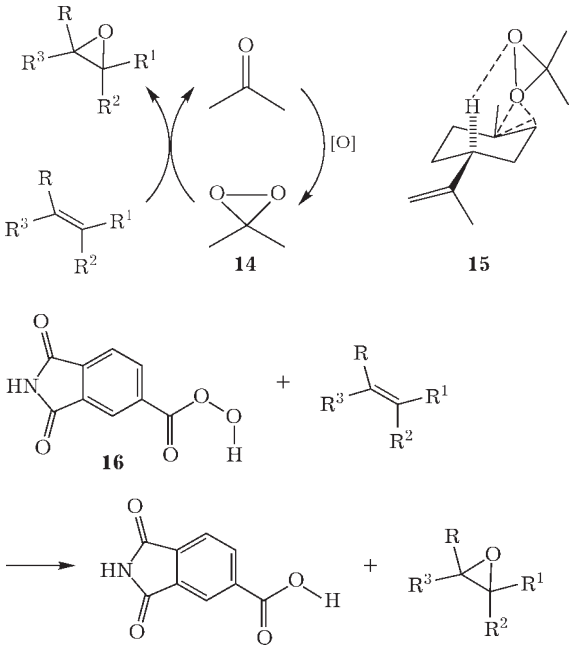


Activator is carbodiimide [67].

Scheme 5.

the works mentioned do not allow one to estimate technological parameters of this scheme.

Two very efficient epoxidizing agents are known such as dimethyldioxirane **14** and 5-hydroperoxycarbonylphtalimide **16**. Their action is demonstrated in Schemes presented below. In the first case intermediate species **15** is presented at the instant of limonene attack by compound **14**.

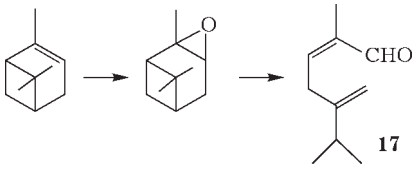


Judging from small number of publications, a wide application of compounds **14** and **16** is prevented by the complications in the synthesis of these epoxidizing agents.

Some authors studied parallel reactions of terpenes epoxidation and their oxidation with the conservation of the cyclohexane fragment. Regarding publications the latter direction was the main one [72–74]. In this case researchers varied the conditions to aim at achieving the maximal yield of verbenone [75] or campholenic aldehyde [76].

Let us consider in brief the publications devoted to the biochemical epoxidation. In publications [14, 15] the source of active oxygen is presented by percarbonic acid or its ester obtained *in situ* from dimethylcarbonate in the presence of hydrogen peroxide and immobilized lipase. Good yields of epoxides of α- and β-pinene were achieved amounting to 85 and 77 % at the temperature of 20 and 40 °C, respectively. However, the reactions of dimethylcarbonate and lipase obtaining represent rather complicated processes, whereas for the epoxidation a great amount of enzyme and a fivefold excess of 60 % hydrogen peroxide solutions are used. The switching to immobilized lipase (Novozyme 435) and to hydrogen peroxide complex with urea [20] has allowed the researchers to lower essentially the consumption of the reagents mentioned with achieving 95 % yield of 2,3-epoxypinane. The authors of [16] carried out the oxidation of *R*-(+)-α-pinene and *S*-(+)-limonene using preparations based on cytochrome R 450cam. The selectivity of the processes and the yield of epoxides was very low, and one could consider a high (>95 %) diastereoselectivity of the process to be the only achievement.

The authors of [17] investigated the synthesis of isonovalol:



From the authors' standpoint, compound **17** is of interest for the manufacture of fragrance compounds. The biomass of *Pseudomonas rhodesiae* PF1 (biocatalyst) is cultivated on a nutrient medium containing α-pinene. The enzyme-catalyzed stage of isonovalol **17** formation follows after the synthesis of epoxide.

In the works [18, 19] the epoxidizing agent is presented by peroxyoctanoic acid which is formed *in situ* from an approximately equimolar amount of octanoic acid and hydrogen peroxide in the presence of immobilized lipase. Toluene and water were used as solvents. As much as ~65 % of terpene was consumed in the presence of 7–8 mass % of the catalyst, 150 mol. % (with respect to α-pinene) of 35 % hydrogen peroxide in the mixture during 3 h at a room temperature. The influence of many factors was investigated: the origin of lipase, its charge, the concentration of hydrogen peroxide and the rate of its feeding into the reaction medium, the concentration of source octanoic acid, and the temperature. The method described did not provide stable results; it is characterized by authors only as an alternative one. Nevertheless, it is obvious that the development of biochemical methods for epoxidation is rather promising, since the syn-

thesis of many bioactive substances in the wildlife occurs through epoxide intermediate species.

In summary attention should be drawn to an original synthesis of two-layer membranes, those allow separating the racemic mixture of chiral epoxides with a simultaneous formation of enantiomerically pure diols [77].

Particular conditions and results of the epoxidation reactions are presented in Tables 3–6.

CONCLUSION

The review of the literature concerning the methods for the epoxidation of terpenes indicates that there is unrelenting, but selective researchers' interest in this reaction. So, if six articles and patents per year are on the average devoted to the formation of the oxirane ring in α-pinene and limonen, one or two publications a year are devoted to similar modifying of β-pinene and 3-carene.

The overwhelming majority of the methods for the epoxidation of the terpenes under consideration are catalytic ones, which reflects the general tendency of chemical technology development. As main epoxidizing agents one uses to apply hydrogen peroxide and oxygen those yield for the most part environmentally compatible by-products.

Despite of the abundance of methods for the synthesis of epoxides, only few among them could be considered to be a basis for the organization of the process for the manufacture of terpenoids. The present review elucidates the following two reasons of such circumstances. First, the efficient catalysts are either inaccessible due to scarcity (for example, methyltrioxorhenium), or are complicated with respect to the structure and the methods of obtaining (for example, polyoxometallates). Second, there are no rational flow sheets for the processing of epoxidation reaction mixtures presented in the literature with the isolation of target products and recycling of by-products. In this connection the published data allow only preliminary planning of promising systems in order to obtain either epoxide. To what extent could the reaction pathways chosen result in a technological, economical, low-waste, environmentally compatible process one might found out only in the studies concerning "tail" operations.

According to our opinion, the following systems could be assigned to a number of promising ones for use in the epoxidation of terpenes:

1. A number of combinations based on methyltrioxorhenium activated by any aromatic nitrogen-containing compound (pyridine, imidazole, *etc.*). With the use of this system the conversion level for different terpenes and the yield of epoxides amounts to 89–98 % in homogeneous, immobilized and incapsulated forms under the action of a small excess of 30–35 % hydrogen peroxide solution.

2. A system able to epoxidize a number of terpenes in an aqueous organic solution of sodium bicarbonate activated with catalytic amounts of manganese sulphate and salicylic acid. Polar solvents containing no halogens are used as an organic component of the medium. Such a system is cheap, readily available, compatible with the environment, however it requires for a multiple excess of 30–35 % H_2O_2 solution as well as recycling of spent solutions.

3. A system based on V_2O_3, which is attractive due to the simplicity of epoxidation procedure and the availability of reagents. The reaction occurs with a small excess of 30 % hydrogen peroxide solution in the presence of small amounts of simple salts (mainly phosphates and QAS), with moderate yields of epoxides. The universality of this system is not quite clear; the use for many terpenes is under patenting, however, the examples are presented only for 3-carene and limonene.

4. The synthesis of α-pinene and limonene epoxides with the yields of 90–98 % could be carried out with the help of Mn porphyrin catalysts activated with alkylimidazole or isobutyl aldehyde. In this case the porphyrin cycle should contain benzene or pyridine substituents. Simple epoxidizing agents (such as water, hydrogen peroxide, oxygen) are used. The main problem arising in the use of this system consists in the obtaining of a catalyst.

5. Unique positive results are produced with the use of some catalytic systems based on polyoxometallates. One could offer the examples of α-pinene epoxidation catalyzed by polyoxometallate without vanadium, nevertheless with activators (amines, silane derivatives, dibenzyl) and immobilized polyoxometallate containing cobalt (the activator representing isobutyl

aldehyde). In both cases under very soft conditions the technological parameters amounted to 90–96 %. The system under discussion was successfully used for 3-carene, too.

One should pay attention to the epoxidation in fluorinated solvents without catalysts. Such terpene as α-pinene in perfluorohexane medium in the presence of *iso*-aliphatic aldehyde reacts to result in the formation of an epoxide derivative with technological parameters of 90–95 % during 4 h at a room temperature in the flow of oxygen. Much better results under equally soft conditions were obtained for the epoxidation of limonene and 3-carene. However, the source of active oxygen in the first case is presented urea complex with hydrogen peroxide, whereas in the second case 60 % solution of the latter is used.

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LIST OF ABBREVIATIONS

QAS – quaternary ammonium salt
DCC – dicyclohexyl carbodiimide
RM – reaction mixture
MTO – methyltrioxorhenium
US – ultrasound
TCICA – trichloroisocyanuric acid
Mn(TPyP) – Mn tetrapyridineporphyrin complex
EDTA – ethylenediaminetetraacetic acid
TBA – tetrabutylamine
EA – ethyl acetate

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