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Assessment of MTO as a catalyst for the synthesis of acid sensitive epoxides. Use of the biphasic system H_2O_2/CH_2Cl_2 with and without bipyridine and influence of the substituents on the double bonds

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Abstract

Methyltrioxorhenium (MTO) catalyzes the selective epoxidation of alkenes in the biphasic medium CH_2Cl_2/H_2O_2–H_2O. Especially sensitive epoxides, which could not be obtained by the use of other reagents, have been isolated in high yield by the addition of bipyridine to this reaction medium.

Keywords: Methyltrioxorhenium (MTO); Epoxides; Diols

1. Introduction

Attempts to transform stoichiometric reactions into catalytic processes are under active investigation. This is, for example, the case for the oxidation reactions of organic compounds: though industrial transformations of olefins into epoxides involve the use of catalysts associated with either oxygen, hydrogen peroxide or organic peroxides, stoichiometric reactions are still commonly used for the oxidation of fine chemicals. [1] An important improvement in this field arose with the discovery by Herrmann et al. [2,3] of methyltrioxorhenium (MTO) which has been found as one of the most effective catalysts for the epoxidation of non-activated olefins in the presence of aqueous hydrogen peroxide. This reaction is usually carried out in an homogeneous medium and uses *t*BuOH as solvent. A drawback of this system is the easy transformation of the epoxides into diols under these conditions. Attempts to limit these deleterious side reactions can already be found in the literature.

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[1] For a recent account see for example, Ref. [1].

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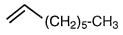
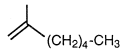
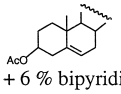
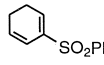
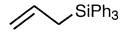
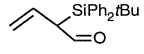
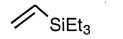
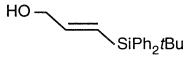
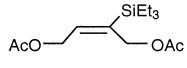
Indeed, the use of tertiary amines [4] or of the urea/H_2O_2 complex instead of aqueous hydrogen peroxide [5,6], and more recently, the use of pyridines [7,8] as an additive which not only protects the epoxides from their transformation into diols but also accelerates the oxidation process, improved greatly the selectivity of the transformations carried out with this new reagent.

The purpose of this paper is to report on our observations and conclusions in this field and first to describe the use of MTO in the biphasic CH_2Cl_2/H_2O_2 medium, to establish the possibilities and the limits of this system for the preparation of acid-sensitive epoxides, in the absence and in the presence

Table 1

entry	substrate	time (h)	temperature	conversion (%)	selectivity (%)
1		1	RT	96	>99
		2	RT	100	>99
2		1	4°C	92	93
		2	4°C	98	86
3		29	RT	95	100
4		2	RT	98	96
5		2	4°C	80	100
		3	4°C	86	85
	+ 6% bipyridine	2	RT	99	95
6		2	RT	70	50
	+ 6% bipyridine	1	RT	55	99
7		.5	0°C	60	90
8		2	4°C	99	99
9		3	0°C	100	100
10		2	4°C	57	95
	+ 6 % bipyridine	2	RT	94	95
11		24	RT	75	95
		54	RT	87	60
12		19	RT	98	85
13		24	RT	55	95
14		24	RT	20	99
15		48	RT	27	99
16		24	RT	0	

of amines, the role of which will be stressed. Secondly, some examples of the epoxidation of encumbered olefins will demonstrate that despite the general scope of the use of MTO as an epoxidation catalyst, limitations inherent to the reagent can be found.

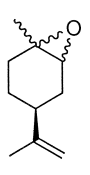
2. Results and discussion

The epoxidation of a series of simple olefins by the homogeneous system discovered by Herrmann et al. [2,3], which involves MTO/H_2O_2/*t*BuOH has been described both in a patent and in several publications: although epoxides could be isolated in several instances, diols resulting from the interaction of water with the epoxides, under the influence of H_2O_2 (a Bronsted acid) and of MTO (a Lewis acid), were very often observed. Since MTO is soluble both in water and in organic solvents, the contact of the epoxides with water has to be avoided after their formation: this could be achieved by using a biphasic dichloromethane/hydrogen peroxide system which in turn makes the work-up easier, a point which is important for sensitive epoxides.

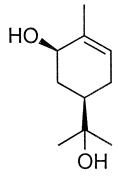
2.1. MTO / H_2O_2–H_2O / CH_2Cl_2 for the epoxidation of simple olefins

The possibilities of this system were first checked with simple olefins (Table 1) [8]. [2] Thus cyclooctene, which is very efficiently oxidized by MTO/H_2O_2–H_2O/*t*BuOH and leads to an epoxide stable under these reaction conditions, gave a 100% yield of the epoxide at room temperature after 2 h: this is a very fast reaction, the conversion being already 96% after 1 h. The conversion and the yield are equivalent for the two systems, but the biphasic system is slightly slower.

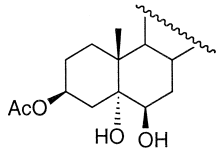
Several other olefins which lead to mixtures of epoxides and diols with the homogeneous system gave excellent conversions with high selectivities for the epoxide with this new system: this was the case for limonene which gave a 1:1 mixture of the two isomeric monoepoxides **2a**, 1-octene, cyclohexene, and citronellal. In these three cases, the reaction simply had to be carried out at 4°C instead of room temperature in order to avoid the formation of the corresponding diol.



2a



7a



10a

2.2. MTO / H_2O_2–H_2O / CH_2Cl_2 / bipyridine

A series of olefins which are more sensitive to acids and water led, even in the case of the biphasic system, to mixtures of epoxides and diols; this was the case for cyclohexene, at room temperature, for α- and β-pinenes (among the products formed from α-pinene, sobrerol **7a**, the hydrolysis/rearrangement product of the corresponding epoxide, could be isolated and characterized by comparison with

[2] Preliminary results were disclosed by A. Deloffre and J. Gregorio at the Société Française de Chimie Meeting (1994), Lyon, France.

an authentic sample), and for citral. In these cases, the biphasic oxidation reaction had to be carried out in the presence of 6% bipyridine, an additive which had already been used by Herrmann et al. [4] in the homogeneous system: high selectivities in the epoxides were again observed (entries 5 and 7–9).

The case of cholesteryl acetate was interesting: at 57% conversion (2 h), the formation of a mixture of epoxides without diols was observed. However, longer reaction times aimed at improving the conversion led to the formation of the 5α,6β-diol **10a**. An important improvement of the selectivity was nevertheless observed when bipyridine (6%) was added to the reaction mixture (94% conversion; 95% epoxide selectivity).

The presence of a deactivating sulfonyl group in the diene gave, with the biphasic system, the expected epoxide of the disubstituted double bond with 95% selectivity at 75% conversion (entry 11 see Section 4).

2.3. Influence of the substituents on the double bonds. Limits of the method

Up to now we have examined the case of simple olefins. The influence of the substituents on the stereochemical outcome of the reactions could, however, already be observed in the case of cholesteryl acetate: the approach of the reactant (in the present case the diperoxo complex) took place preferentially from the less hindered side of the molecule. Nevertheless, the overall yield of the reaction remained high. This was, however, not the case for the following series of unsaturated silanes (entries 12–16). Thus triphenylallylsilane gave the expected epoxide with high conversion (98%) and good selectivity (85%) (entry 12). Crowding the double bond by the introduction of a formyl group decreased the conversion to 55% giving the expected acid-sensitive epoxide (entry 13). Interestingly, according to the ^{1}H NMR spectrum, the reaction took place with complete diastereoselectivity. When the trisubstituted silicon atom was directly linked to the double bond, the yield of epoxide dropped considerably (20%, entry 14). The introduction of an extra substituent (entry 15) led to an even worse result: only 10% conversion to the epoxide was observed after three days under the standard biphasic conditions. In order to improve the conversion to 27%, both the amounts of MTO (5%) and of H_2O_2 had to be increased. It is important to notice at this point that the corresponding epoxide could nevertheless be prepared quantitatively by using meta-chloroperbenzoic acid as epoxidation reagent. [3] The trisubstituted unsaturated silane (entry 16) was even more reluctant to react: no epoxide at all could be detected, the starting material being recovered after 24 h.

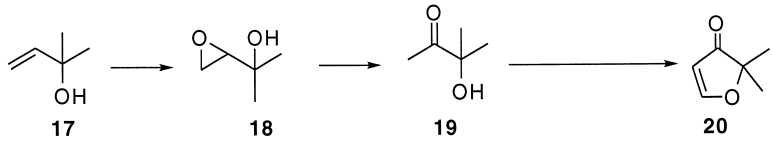
The low yield of these transformations might be assigned to an interaction (with deactivation) of MTO with the silicon atom. However, neither could such an interaction be detected by NMR spectroscopy (no modification of the spectrum of a mixture of the vinyl silane and of MTO), nor was an MTO-induced decomposition of the starting material observed. It is therefore likely that the poor reactivity observed when the number of substituents of the double bond in this series of compounds is increased, is inherent to the size of the reagent, the diperoxo complex.

2.4. Acid-sensitive olefins and epoxides: tuning of the reaction conditions. MTO-induced rearrangement of epoxides

Most of the epoxides described so far can be prepared in high yield and with good selectivity by the use of more classical epoxidation reagents such as perbenzoic acids.

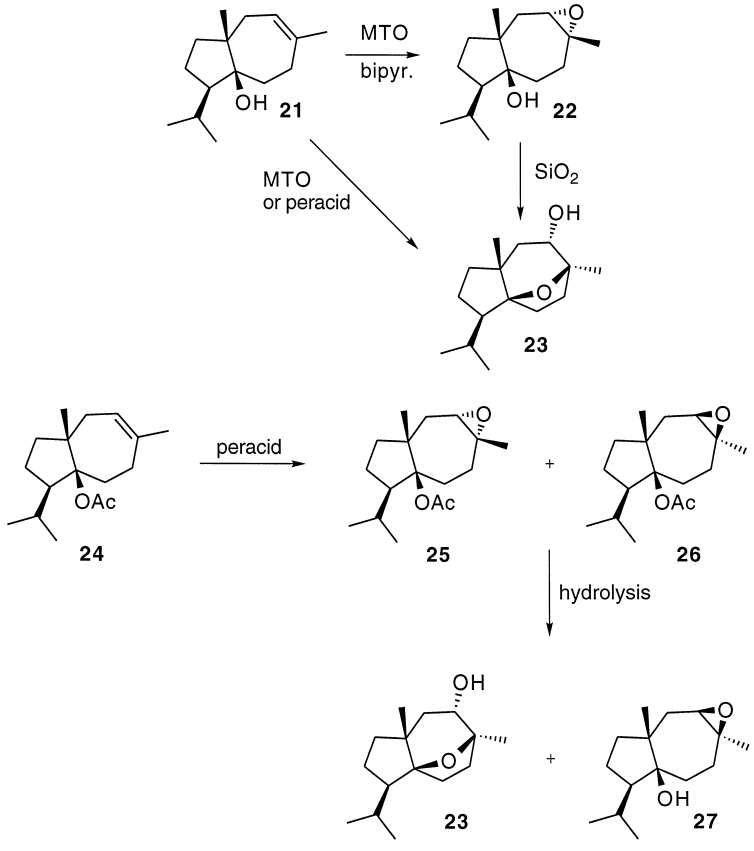
[3] Observation from this laboratory.

Examples of less stable olefins and epoxides can however be found in the literature: they are either very sensitive to acids or cannot be prepared in satisfactory yields by the use of classical methods. Among them, we chose to attempt the synthesis of a series of three epoxides: (i) the epoxide of 2-methyl-3-buten-2-ol **17**, a tertiary allylic alcohol which rearranges easily under acidic conditions; this epoxide is an interesting intermediate, useful in organic synthesis since it is easily isomerized to the hydroxy ketone **19** [10] the starting material for the preparation of the lactone **20** [11,12]; (ii) the epoxide of the sesquiterpene carotol **21**, a natural product from the seeds of carrots utilized in the food industry, which cannot be synthesized by the use of classical peracid oxidation reactions: its preparation constitutes thus a challenge [13]; (iii) finally, linalyl epoxide **29** [14–16], which can be obtained from linalool **28**, and which easily undergoes an intramolecular reaction leading to linalyl oxide **30**, an important starting material for fragrances.



17 18 19 20

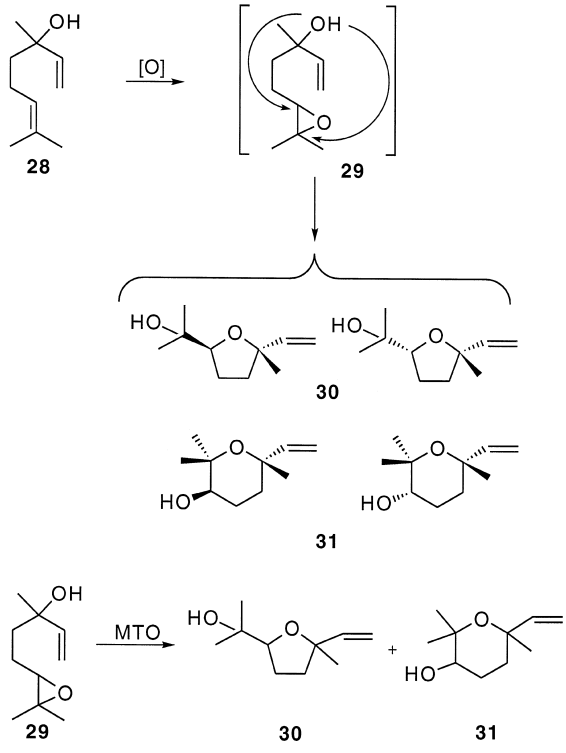
The oxidation of the tertiary allylic alcohol **17** under the biphasic conditions led, after 24 h at room temperature, to the expected epoxide **18** in 90% yield with 100% selectivity, thus a considerable improvement on the homogeneous system which gave only 50% conversion of the olefin with 20% epoxide selectivity.



The second alcohol, carotol **21**, is known to give daucol **23** upon reaction with perbenzoic acid, probably via the unstable, selectively formed *trans* epoxide **22** [13]. This result is due to the existence of a hydrogen bond between the hydroxyl group and the carbon–carbon double bond which hinders the approach of the oxidizing agent from the side of the hydroxyl group. With MTO in the biphasic system, a quantitative yield of daucol was also obtained, probably via the same intramolecular reaction. The same result was observed with the homogeneous system: daucol **23** was reproducibly formed in yields between 92 and 100%. This result confirms the high sensitivity of the presumed hydroxy–epoxide **22** towards acids.

The addition of six equivalents of bipyridine to the biphasic system at 0°C, completely changed the course of the reaction: conversions of 95% were achieved with selectivities of 85–90% for a new product the structure of which agreed with that of the *trans* epoxide of carotol **22**. Indeed, attempts to purify it by silica gel chromatography led exclusively to the formation of the more polar daucol **23**: thus a weak acid such as silica gel was able to promote the rearrangement of the intermediate epoxide **22**. Such a transformation had already been observed [13] starting from a mixture of **25** and **26**, the *cis* and *trans* epoxides of carotol acetate **24**, which gave after saponification a mixture of daucol originating from the *trans* epoxide **22** via an intramolecular oxirane opening and of *cis* epoxide arising from the *cis* epoxy–acetate **26**. The ^{1}H NMR spectrum of the new epoxide is very close to that of the previously described epoxide **27**, the signal for the gem–proton on the carbon bearing the oxygen atom appearing as a triplet at δ2.78 ppm (triplet at δ2.68 for the *cis* epoxide **27**).

As a third example of olefins leading to highly reactive epoxides, we choose linalool **28** which contains both a terminal and a trisubstituted double bond. This diene is known to lead with organic peracids to the acid-sensitive diastereomeric epoxides **29**, which very easily rearrange to a mixture of hydroxyfuranes **30** and hydroxypyranes **31** by an intramolecular reaction akin to that observed in the case of carotol.



With MTO in the biphasic medium at 4°C, linalool is completely converted into a 2:1 mixture of **30** and **31**. No epoxide **29** could be detected. However, in the presence of bipyridine at room temperature the formation of the epoxide was observed (10%) together with the furanes and the pyranes. At 4°C the conversion was very low, the major product of the reaction being nevertheless the epoxide **29**. The homogeneous system led also in high yield to a 2:1 mixture of **30** and **31**. Therefore, the preparation of the epoxide in satisfactory yield proved difficult due to the lower reactivity of the trisubstituted double bond of linalool. In this and the previous case, the hydroxyl group, which is thought to interact with the oxirane, is already present in the molecule: coordination of free MTO and/or of the peroxo rhenium species to the oxygen atom of the epoxide would then be able to induce an intramolecular reaction.

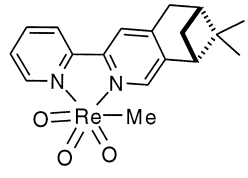
We confirmed that MTO was acidic enough to induce such a rearrangement of the epoxides **29**. These epoxides were prepared in high yield by the aerobic oxidation of linalool in the presence of isobutyraldehyde and Co (**II**) tetraphenylimidodiphosphinate ($Co(TPIP)_2$) as catalyst [9]. Thus, in the presence of 1% of MTO, in dichloromethane, and at room temperature, a 2:1 mixture of **30** and **31** was obtained quantitatively from **29**.

2.5. Remarks on the reaction of MTO with tertiary amines

Many tertiary amines (aromatic or non-aromatic) are known to interact with MTO to give 1:1 adducts [4]. We showed that in the case of triethylamine, this interaction was more complex. Indeed, according to the ^1H NMR spectrum of a 1:1 mixture of this amine and MTO in dichloromethane, a fast reaction leading to a red complex took place: disappearance of the methyl group of MTO was observed together with a downfield shift of the methylene protons of the amine and the appearance of a broad signal at δ 6.5 ppm (Et_3NH^+?). Unfortunately, this new complex could not be further characterized due to its instability. A reasonable explanation for this observation would be a deprotonation of MTO, the fate of the methylene group being, however, unknown.

Other amines can act as a reductant of MTO: this is for example the case for picolinic acid (PICH) which reacts slowly with MTO at room temperature to give the Re(V) complex $MeReO(PIC)_2$ [17].

As far as the oxidation reactions in the presence of amines are concerned, we demonstrated by ^1H NMR that partial oxidation of bipyridine in the presence of MTO and H_2O_2–H_2O takes place leading to 2,2′-bipyridyl-*N*,*N*′-dioxide. The oxidation of amines by the MTO/ H_2O_2–H_2O system has recently been reported [18].



32

Since bipyridine is known to give a stable complex with MTO, and since this complex is active in the epoxidation reaction of olefins, we synthesized a well defined optically active complex **32** starting from an equimolecular amount of MTO and the chiral bipyridine (−)-(4,5)-pinenebipyridine (yellow complex, mp 109°C) [19] and used it for the epoxidation of 2-methyl-1-heptene which might lead to chiral epoxides. However, although the epoxidation reaction took place, no enantioselectivity was observed so far.

3. Conclusion

The results described herein demonstrate the great possibilities of MTO as a precursor for the epoxidation of olefins and its use for the preparation of fine chemicals. We found that the synthesis of moderately sensitive epoxides can be carried out simply by using the biphasic $MTO/CH_2Cl_2/H_2O_2–H_2O$ system to avoid contact of the epoxides with water, and by tuning the experimental conditions. For more sensitive epoxides, the addition of an amine such as bipyridine inhibits the formation of by-products such as diols: this system was used with success for the preparation of previously unknown epoxides. Finally, a great achievement with this system remains a goal, the enantioselective epoxidation of olefins. Unfortunately, attempts conducted in this direction were up to now unsuccessful.

4. Experimental

4.1. General methods

^1H NMR and ^{13}C NMR spectra were recorded on a AC 200 or ARX 400 Bruker spectrometer. IR spectra were recorded on a Perkin-Elmer 1420 spectrophotometer. Mass spectra were recorded on a ZAB HSQ (Fisons) instrument. Column chromatography was performed with Merck silica gel (70–230 mesh) using various ratios of ethyl acetate/light petroleum ether or dichloromethane/light petroleum ether as eluent. GC was carried out on a Girdel 30 chromatograph with an OV1701 (Quadrex) column (50 m, 0.25 mm). For the separation of enantiomers, a CP-Chirasil-DEX CB column was used.

MTO was prepared by a slightly modified version of the published method starting from 10 g of Re_2O_7 in an overall yield of 85% after silica gel chromatography and recrystallization.

The simple epoxides were compared to authentic samples by their physical data (retention time, NMR spectra).

4.2. Epoxidation reactions: general methods

4.2.1. MTO / H_2O_2–H_2O / CH_2Cl_2

Six millimoles of olefin in dichloromethane (5 ml) were stirred at the desired temperature for a few minutes. For the reactions carried out in the presence of bipyridine, six equivalents vs. MTO of bipyridine were added. MTO (1 mole%/olefin) was then added to the solution which turned yellow in the presence of bipyridine. One hundred fifty equivalents of H_2O_2 (10%) were then added with vigorous stirring. The mixture turned yellow (even in the absence of dipyridine). The progress of the reaction was monitored by either GC or TLC and analyzed after quenching with MnO_2.

4.2.2. MTO / H_2O_2 / tBuOH

MTO was dissolved in *t*BuOH (1 ml) at $-20°C$. Then the olefin (100 eq) and H_2O_2 in *t*BuOH were added successively to the catalyst solution and the mixture stirred at $-16°C$. Excess H_2O_2 was destroyed by MnO_2 and the organic products extracted with dichloromethane.

4.3. Epoxidation of α-pinene

Besides the expected epoxide, a very polar product was isolated and identified as sobrerol **7a** by its ^1H and ^{13}C NMR spectra. ^1H NMR ($CDCl_3$, 200 MHz) δ 5.56–5.53 (dd, 1H), 4.04–4.01 (t, 1H),

2.18–1.97 (m, 2H), 1.80–1.62 (m, 7H), 1.47–1.31 (m, 1H), 1.20 and 1.17 (2s, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 134.45, 125.33, 72.36, 68.65, 38.98, 32.66, 27.83, 26.12, 20.93.

4.4. Epoxydation of (cyclohexa-1,5-dienesulfonyl)-benzene

The epoxide was obtained as a white solid (mp 89°C) in 75% yield after silica gel chromatography (eluent: dichloromethane/petroleum ether 1:1). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.93–7.89 (d, 2H), 7.63–7.55 (m, 3H), 7.18–7.15 (d, 1H), 3.67 (s, 1H), 2.35–2.08 (m, 3H), 1.76–1.57 (m, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 142.00, 140.28, 138.88, 133.93, 129.81, 128.19 (Ar, C=C), 55.09, 45.88, 21.19, 19.96. MS calcd for $C_{12}H_{12}O_3S$, 236 (M^+); found 236.

4.5. Epoxidation of cholesteryl acetate

For the epoxidations carried out in the absence of bipyridine, besides a mixture of α- and β-epoxides, monoacetate of cholestanetriol **10a** was isolated and characterized as a white solid, mp 207°C (lit. 207 °C) [20]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.18–5.11 (m, 1H), 3.57–3.55 (d, 1H), 2.21–2.13 (t, 2H), 2.03(s, 3H), 2.01–0.86 (m, 40H), 0.69 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.14, 76.30, 75.72, 71.88, 56.40, 55.92, 45.42, 42.83, 39.90, 39.88, 38.38, 36.95, 36.37, 35.94, 34.63, 32.68, 31.48, 28.58, 28.30, 28.10, 24.32, 24.05, 22.92, 22.77, 22.18, 21.63, 18.77, 16.79, 12.25. Anal. Calcd for $C_{29}H_{50}0_4$: C, 75.32; H, 10.82. Found: C, 75.28; H, 10.90.

*4.6. Epoxidation of 2-methyl-3-buten-2-ol (**17**)*

The epoxide was obtained in 90% yield and compared with an authentic sample by GC and NMR spectroscopy. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.90–2.87 (t, 1H), 2.76–2.72 (q, 1H), 2.68–2.64 (t, 1H), 2.32–2.22 (1H, OH), 1.22 (s, 3H), 1.16 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz), δ 67.68, 58.36, 44.20, 27.59, 24.79.

*4.7. Epoxidation of carotol (**21**)*

Carotol was oxidized in the presence of bipyridine to give a 95% yield of a mixture of *trans* (98%) and *cis* (2%) epoxides of carotol. After extraction as usual, the epoxides were analyzed by NMR spectroscopy. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.78 (t, $J = 6.6$ Hz, *trans* epoxide), 2.68 (t, 1H, $J = 6.5$ Hz, *cis* epoxide), 1.80–1.40 (m, 12H), 1.30 (s, 3H), 1.04 (s, 3H), 0.80 (t, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 84.99, 60.60, 50.09, 48.54, 41.06, 40.04, 39.63, 31.17, 29.34, 27.45, 24.12, 23.55, 23.10, 21.39, 20.35.

Attempts to purify the epoxide by silica gel chromatography gave quantitatively daucol **23** as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.77–3.73 (dd, 1H), 2.21–2.14 (m, 1H), 1.91–1.69 (m, 5H), 1.61–1.48 (m, 2H), 1.38 (s, 3H), 1.32–1.26 (m, 4H), 1.08–1.06 (d, 6H), 0.82 (d, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ 91.73, 85.40, 71.63, 52.50, 45.85, 41.11, 41.17, 33.05, 31.55, 29.51, 26.49, 23.54, 23.02, 22.47, 21.86.

*4.8. Epoxidation of linalool (**28**)*

The linalyl epoxides **29** were obtained upon oxygen oxidation of linalool (0.435 g), in dichloroethane (5 ml) in the presence of isobutyraldehyde (excess, 1.5 ml) and $Co(TPIP)_2$ as an oil (0.30 g) after

silica gel chromatography. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.92–5.74 (m, 1H), 5.20–5.11 (d, 1H), 5.02–4.97 (d, 1H), 2.71–2.68 (t, 1H), 1.68–1.45 (m, 5H), 1.29–1.08 (m, 9H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 144.88, 112.14, 72.88, 64.66, 59.23, 38.66, 28.04, 27.87, 24.89, 23.61, 19.92, 18.92, 18.69.

The furanes and the pyranes **30** (67%) and **31** (33%) were obtained quantitatively from linalool, MTO and H_2O_2 in dichloromethane, in the absence of bipyridine. Physical data for **30**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.02–5.86 (dd, 1H), 4.99–4.98 (d, 1H), 3.44–3.37 (t, 1H), 2.12–2.07 (m, 1H), 1.73–1.50 (m, 4H), 1.22 (s, 3H), 1.14 (s, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 146.37, 110.71, 76.03, 74.90, 73.54, 32.55, 31.72, 29.68, 25.71, 20.88. Physical data for **31**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.03–5.89 (dd, 1H), 5.22–5.13 (dd, 1H), 5.02–4.96 (dd, 1H), 3.87–3.82 (t, 1H), 2.12–2.07 (m, 1H), 1.91–1.74 (m, 4H), 1.30 (s, 3H), 1.22 (s, 3H), 1.11 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 145.95, 11.65, 85.68, 71.43, 37.96, 27.58, 26.54, 26.06, 24.36.

*4.9. Epoxidation of triphenylallylsilane (**12**)*

Physical data of the epoxide obtained as an oil after silica gel chromatography (eluent diethyl ether/petroleum ether 5/95): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57–7.55 (m, 6H), 7.45–7.38 (m, 9H), 3.16–3.13 (m, 1H), 2.69–2.67 (t, 1H), 2.37–2.35 (dd, 1H), 2.16–2.11 (dd, 1H), 1.44–1.38 (dd,1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.64, 134.12, 129.87, 128.12, 50.16, 49.21, 18.46. MS calcd for $C_{21}H_20OSi$, 316. Found: 259 $(M-57)^+$.

*4.10. Epoxidation of the silane (**13**)*

Due to its instability on silica gel, this epoxide could only be characterized by its ^{1}H NMR spectrum ($CDCl_3$, 200 MHz) δ 10.08 (d, 1H), 3.55–3.52 (m, 1H), 2.82–2.79 (m, 1H), 2.50–2.48 (m, 1H), 2.21–2.19 (m, 1H).

*4.11. MTO-(−)-(4,5)-pinenebipyridine (**32**)*

MTO (0.10 g) was dissolved in dichloromethane. To this solution, the chiral ligand (0.10 g) was then added. The solution turned yellow. Pentane was added and the solution cooled to −16°C. Yellow silk-like crystals formed (0.15 g), mp 109°C. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 9.02 (d, 1H), 8.59 (s, 1H), 8.31–9.29 (d, 1H), 8.17–8.13 (dt, 1H), 8.12 (s, 1H), 7.62–7.58 (m, 1H), 3.31–3.21 (d, 2H), 3.06–3.03 (t, 1H), 2.86–2.81 (m, 1H), 2.45–2.42 (m, 1H), 1.49 (s, 3H), 1.32–1.30 (d, 1H), 0.96 (s, 3H), 0.73 (s, 3H). ^{13}C NMR (CD_2Cl_2, 50 MHz) δ 149.80, 149.48, 148.34, 147.23, 145.49, 139.81, 132.78, 126.09, 122.87, 122.77, 44.86, 39.77, 39.10, 33.37, 31.29, 26.86, 25.54, 21.24. Anal calcd for $C_{18}H_{21}N_2O_3Re$: C, 43.19; H, 4.21; N, 5.60. Found: C, 43.29; H, 4.18; N, 5.49.

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