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On the way to chiral epoxidations with methyltrioxorhenium(VII) derived catalysts

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Abstract

Methyltrioxorhenium(VII) (MTO) is successfully applied as chiral epoxidation catalysts in the presence of H_2O_2 as oxidizing agent and excess chiral Lewis base ligands derived from pyrazole. Moderate enantiomeric excesses up to ca. 30% can be reached at low reaction temperatures (−30 °C), the conversions however, being quite low (<25%). The reason for this may be the fluctionality of the N-base ligand. Glycolate complexes of MTO, applied under the same conditions reach somewhat higher enantiomeric excesses (up to ca. 40%), however, again associated with low conversions (<30%). In this case the sensitivity of the catalyst to water induced ligand removal as well as to ligand exchange with other diols is the most likely reason. Nevertheless, the enantiomeric excesses reported here are among the best observed for MTO derived catalytic systems reported to date and more active and selective systems seem feasible.

Keywords: Chirality; Epoxidation; Glycolates; Methyltrioxorhenium; Pyrazoles

1. Introduction

Chiral epoxidations are of growing interest for the synthesis of chiral intermediates in pharmaceutical and chemical industry to generate enantiomeric pure products [1]. In 1979, Mimoun and coworkers [2] achieved the enantioselective epoxidation of prochiral alkyl-substituted olefins with a Mo(VI) complex bearing a chiral ligand, but the enantioface selectivity was not high. In 1980, Katsuki and Sharpless [3] reported on the asymmetric epoxidation of allylic alcohols mediated by a titanium(IV) complex using (+)-(R,R) or (−)-(S,S) tartrate as chiral ligands. While the enantioselectivity was very high, the titanium complex had to be applied in stoichiometric amounts. Later, a reduction of the catalyst:substrate ratio of ca. 1:20 to 1:10 was achieved and a X-ray structure of the titanium tartrate catalysts could be presented [4]. More recently, non-functionalized olefins have been examined as substrates and high enantiomeric excesses have been achieved only with chiral salene manganese(III) catalysts [5,6]. Several other attempts to achieve chiral epoxidation, e.g., with Mo and W based catalysts have been made, but usually led only to moderate to low enantiomeric excesses [7–12].

In the non-chiral olefin epoxidation methyltrioxorhenium (MTO) is among the most efficient catalysts [13,14]. It was shown that addition of excess Lewis-bases, particularly monodentate ones, leads to a further significant increase of both activity and selectivity towards epoxides [15–20]. A convincing correlation between log K of the binding constant K of the ligand

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L to MTO and the pk_a of L has been presented as well [21]. This correlation, the steric bulk of the applied chiral Lewis bases and the 1:1 ratio of MTO:chiral Lewis base may explain, why earlier attempts to achieve chiral induction via chiral MTO derivatives of the type MTO·L* (L* = chiral Lewis base ligand) failed, despite the successful isolation and characterization of such complexes [22]. Based on results obtained by Sharpless and co-workers [16] Corma and co-workers [23] reported on chiral nitrogen-base adducts applied in the chiral alkene epoxidation. While reaching conversions between 9% and 59% and epoxide selectivities between 35% and 96% the enantiomeric excesses ranged between 4% and 36% at reaction temperatures between −5 and −55 °C, applying reaction times between 7 and 48 h. Interestingly, Corma and co-workers [23] do not assign the moderate obtained yields to a lack of full coordination of the amines to MTO, but to the intrinsic stereochemical features of the newly formed chiral complexes. They base their assumption of strong MTO–L interactions on the unchanged ^{1}H NMR chemical shift of the in situ formed adducts both at high (RT) and at low (−40 °C) measurement temperatures in deuterated chloroform without H_2O_2 being present. For non-chiral R–ReO_3L type complexes the degree of ligand exchange phenomena is usually based on spectro photometric or ^{17}O NMR spectroscopic evidence [19,24,25]. H_2O_2 is known to oxidize several N-donor Lewis bases to their corresponding N-oxides in the presence of MTO [22,26,27], in several cases even more efficiently than the olefins, so that the actually present catalyst is in these cases an adduct of the N-oxide, where the chiral centre is farther away from the reaction site of the substrate with the peroxide ligand.

In this work, we present several approaches to transform MTO into a chiral catalyst and to use it in chiral epoxidations with H_2O_2 as the oxidant.

2. Results and discussion

2.1. Application on Lewis base ligands

Since pyridine derivatives and pyrazole in olefin epoxidation reactions with methyltrioxorhenium/H_2O_2 as catalyst/oxidant [15–20] show an accelerating effect, we applied chiral derivatives of these ligands in our epoxidation reactions. MTO was dissolved in methylenchloride and a 35% solution of aqueous H_2O_2 was added. At −30 °C the substrate (*cis*-methylstyrene) and excess chiral ligand (12:1 with respect to MTO) was added. The exact conditions of the reactions are described in Section 4. As chiral pyridine derivatives (*S*)-nicotine, 6-chloro-(*S*)-nicotine, 6-hydroxy-(*S*)-nicotine, (*S*)-cotinine, and *trans*-cotinine-4-carboxylic acid have been applied (see Chart 1). All of these reactions give at −30 °C low styrene oxide yields (after 2 h below 10%) and no significant enantiomeric excesses (<5%) are achieved. At higher reaction temperatures (0 °C, RT), the reaction is much faster, but no enantiomeric excesses are observed. It is assumed that an oxidation of the nitrogen atoms to N-oxides occurs. The presence of N-oxides is known to be responsible for low overall yields [17,18,22] and also causes, due to the increased distance a severely diminished influence of the chiral centres on the epoxidation reaction.

In contrast to pyridines pyrazoles are much more stable against transformation to N-oxides or other oxidation products [18]. We therefore synthesized some chiral pyrazole derivatives, which are now more easily accessible particularly due to the work of Brunner and co-workers [28–31]. With a catalyst to substrate ratio of 1:100 and reaction temperatures of −30 °C enantiomeric excess up to 27% are obtained in the epoxidation of *cis*-methyl styrene. However, the product yields remain low (<25% in all cases) and longer reaction times, yielding higher amounts of epoxides are associated with diminished enantiomeric excesses in all observed cases. An overview over the obtained results gives Table 1.

Since Lewis base adducts of MTO are known to be more rigid at lower temperatures and less strongly coordinated at higher temperatures [19,20,24,25] we conclude that opening and closing of one of the Re–N

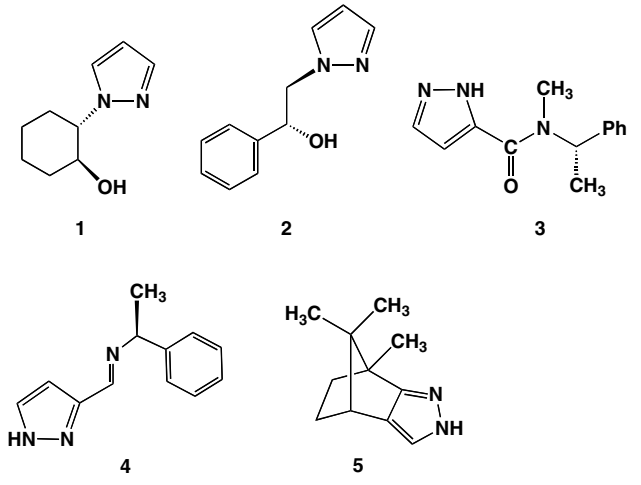


Chart 1.

Table 1
Application of chiral pyrazole based ligands in the catalytic epoxidation of *cis*-β-methylstyrene with MTO/H_2O_2

Ligand	Conversion (%)	Enantiomeric excess (ee)
1	6	27
2	9	12
3	14	10
4	22	15
5	22	6

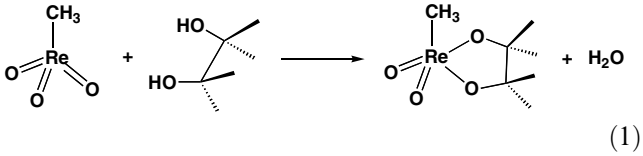
For reaction details see Section 4.

bonds, associated with a ligand rotation may be a plausible reason for the lowering of the enantiomeric excesses at higher reaction temperatures and with increasing reaction time. Similar observations have been made with Lewis base coordinated MoX_2O_2 units [10,11] and with $MoO(O_2)_2$ units coordinated by related ligands [32,33].

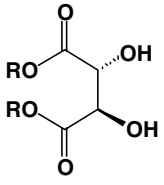
2.2. Application of chiral diols

It is known that vicinal diols react with MTO to form complexes as shown in Eq. (1). The chemical properties of the resulting rhenium(VII) glycolates have been described elsewhere in more detail [34]. As chiral derivatives we chose derivatives of tartaric acid (tartrates), which have been already applied successfully as chiral ligands for other systems [3].

The epoxidation reaction, applying again *cis*-β-methylstyrene as substrate was conducted at reaction temperatures between −30 and −5 °C. The applied catalyst:substrate:oxidant ratio was 1:100:150. The tartaric acid esters have been applied in 12-fold excess with respect to MTO to shift the equilibrium in Eq. (1) on the side of the products. The detailed reaction conditions are given in Section 4. The different ligands applied are shown in Chart 2 as compounds **6**–**12**, the obtained results are summarized in Table 2.



(1)



R=H(6); CH_3 (7); C_2H_5 (8); $CH(CH_3)_2$ (9)

$C(CH_3)_3$ (10); CH_2-C_6H_5 (11); fluorenyl (12)

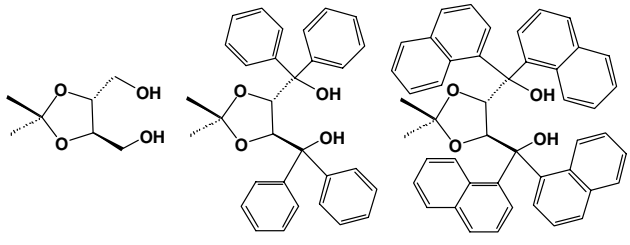


Chart 2.

Table 2
Application of chiral diols in the catalytic epoxidation of *cis*-β-methylstyrene with MTO/H_2O_2

Diol applied	Conversion (%)	Enantiomeric excess (ee)
6	30	5
7	0	0
8	10	11
9	5	18
10	7	15
11	10	15
12	8	16
13	5	41
14	5	15
15	5	14

For details see Section 4.

The catalyst systems lead to epoxide yields between ca. 5% and 30%, with enantiomeric excesses between 5% and 18%. Again, elevated temperatures reduce the enantiomeric excesses and prolonged reaction times, leading to higher substrate conversions also lead to lower enantiomeric excesses. The exceptional low enantiomeric excess of obtained in the presence of excess tartaric acid (**6**) in comparison to its esters **8**–**12** is very likely due to the additional coordination possibility of the ligand through the COOH groups of the tartaric acid. At room temperature it cannot be distinguished between a coordination of the alcohol oxygens or the carboxylic oxygens. In both cases formation of water as a by-product is to be expected. Both sets of protons (—O*H* and —C(O)O*H*) cannot be detected in ^{1}H NMR, although only two of the four O-bound protons are removed due to H_2O-formation (see Eq. (1)). Even at −30 °C no clear distinction can be made, so that the exchange must still be fast on the NMR time scale. In the presence of excess tartaric acid the ^{1}H NMR signals of free tartaric acid and MTO-coordinated tartaric acid can not be distinguished. Only at below −20 °C different signal sets appear in ^{1}H NMR. In the case of the compounds **8**–**12** a similar exchange processes are inhibited (due to the presence of esters, C(O)OR instead of C(O)OH-groups) and the obtained enantiomeric excesses are somewhat higher. However, the formation of water during the course of the epoxidation reaction shifts the equilibrium shown in Eq. (1) increasingly to the side of the starting materials, so that free (un-coordinated) MTO may additionally act as (non chiral) catalyst, thus reducing the enantiomeric excess during the course of the reaction, despite the excess of chiral ligands.

In a further series of experiments a different type of glycols, derived from isopropylidene–threitol has been applied (see compounds **13**–**15** in Chart 2). In this case the diol function is not located on neighbouring carbon atoms, but 1,4 positioned. Under similar reaction conditions as applied for the tartaric acid esters yields up to ca. 40% are obtained, however, again only at low

conversions and low temperatures. It is noteworthy that in the case of the complexes **13**–**15** the bulk of the ligands has a significant influence on the obtained enantiomeric excess while the conversion is not affected. In the case of the complexes **6**–**12** a clear influence of the steric bulk could not be detected. This difference is very likely due to the closer proximity of the bulky ligands in **14** and **15** to the coordination site of the Re core. The bulky ligands seem to block the influence of the chiral centres to a certain degree. In the case of the ligands **6**–**12** the chiral centres are closer to the metal than the varying groups R, which have accordingly less obvious influence on both conversion and ee. Prolonged reaction times and higher reaction temperatures (above 0 °C) lead to lower optical inductions (see Table 2). The steric bulk of the ligands has also a negative influence on the enantiomeric excesses obtained. In contrast to observations made by Sharpless et al. about a positive influence of ageing of the catalyst systems, prolonged waiting times before addition of the oxidation agent to the reaction mixture have a negative effect on the enantiomeric excess in the case of the systems described here. A waiting time of 10 min already leads to a significant reduction of the maximum enantiomeric excess: it drops below 10%. The best results with respect to enantiomeric excesses have been obtained in two-phase systems where the catalyst in located in the aprotic phase. This is not surprising since water, being the by-product of the catalytic oxidation and the solvent of H_2O_2 can destroy the glycolate complexes at prolonged reaction times (see discussion above and Eq. (1)). Furthermore, diols being formed as ring opening products with epoxides under protic conditions can compete with the diol-ligands for coordination to the Re centre. Control experiments have shown that a ligand exchange of Re glycolate complexes of the type examined here with diols is possible at the conditions applied for the catalytic reactions and a temperature increase to room temperature also increases this exchange reaction. Low reaction temperatures (−30 °C) as well as low stirring velocities (due to the diminished reaction of the catalyst with water) prolong the lifetime of the catalyst and lead to higher enantiomeric excesses.

3. Conclusions

Chiral Lewis base ligand adducts of MTO allow to obtain moderate enantiomeric excesses, which are however, associated with generally low overall conversions. Anyway, pyrazole based ligands are – until now – still the best choice for such transformations. The disadvantages of such systems are, however, the high excess of chiral ligand needed and the ligand fluctionality diminishing the enantiomeric excesses. The latter problem can be at least partially overcome at low reaction temperatures, but low overall yields and slow reaction velocities are unavoidable in this case. Chiral diol ligands can also be applied, leading to chiral rhenium glycolate complexes. These compounds are, however, somewhat sensitive to water and can exchange their glycolate ligands with other diols. Both problems can be (partially) overcome at low reaction temperatures, but again, moderate enantiomeric excesses are associated with low conversions and low product yields. A superior reaction system should be therefore, water free (which is difficult to realize with H_2O_2 as oxidant) or display its chiral function on a ligand, which does not easily exchange or react under catalytic conditions, even at room temperature. This may be feasible e.g. with chiral R^*–ReO_3 complexes. Considering the good activity of MTO based systems even at low reaction temperatures and the applicability of the ''green'' oxidation agent H_2O_2 instead of *t*-BuOOH further work in this direction seems to be desirable and is currently under way in our laboratories.

4. Experimental

4.1. General remarks

All preparations and manipulations were done using standard Schlenk techniques under an atmosphere of nitrogen. Solvents were dried by standard procedures (THF, *n*-hexane and Et_2O over Na/benzophenone ketyl; CH_2Cl_2 and NCMe over CaH_2), distilled under nitrogen and used immediately (THF) or kept over 4 Å molecular sieves (3 Å for NCMe). MTO was synthesized according to literature procedures [35,36] the ligands were purchased from Aldrich or Fluka or prepared as described elsewhere [29,30,34].

Microanalyses of the obtained products were performed in the Mikroanalytisches Labor of the TU München in Garching (Mr. M. Barth). Mid-IR spectra were measured on Bio-Rad FTS 525 spectrometer using KBr pellets. ^{1}H NMR, spectra were obtained using a 400-MHz Bruker Avance DPX-400 spectrometer. Catalytic runs were monitored by chiral GC methods on a Hewlett–Packard instrument HP 5890 Series II equipped with a FID, a Supelco column Alphadex 120 and a Hewlett–Packard integration unit HP 3396 Series II.

4.2. Synthesis of MTO adducts with chiral N-bases (general procedure)

Two hundred and fifty milligramme (1 mmol) of methyltrioxorhenium is dissolved in 10 ml CH_2Cl_2 and 1.1 mmol of the respective Lewis-base is added under vigorous stirring at room temperature. The reaction mixture turns from colorless to yellow or orange and in most cases a precipitate of yellowish colour forms im-

mediately. The reaction mixture is additionally stirred at room temperature for 30 min. The reaction solution is then filtered off through a canula equipped with a Whatman filter and the solvent (of the filtrate) is cooled overnight to −40 °C. The precipitates are unified and washed repeatedly with cold, dry pentane. The MTO Lewis base adduct complexes are received yellow solids in yields between 60% and 98%. The elemental analyses are in accord with the expectancies for mono-Lewis base adducts in all cases. Experimental data for three selected compounds are given below.

4.3. Characterization of compounds **1a**, **3a**, and **5a** (reaction products (MTO-Lewis base adducts) of the ligands **1**, **3**, and **5** with MTO)

4.3.1. Compound **1a**

^{1}H NMR (CD_2Cl_2, RT, ppm): 7.56 (CN(N)–C*H*, d, 1H); 7.40 (NCHC*H*CHN, dd, 1H); 6.36 (Re–NC*H*CH, d, 1H); 3.9–3.7 ((N)C*H*–C*H*(O*H*), m, b, 3H); 2.26 (Re–CH_3, s, 3H); 2.14–1.39 (CH_2, m, 8H); IR (KBr, *v*, cm^{-1}): 3260 m,b (OH), 3110 m, 2991 w, 2935 st, 1470 w, 1296 w, 972 m, 946 st (Re=O), 760 m; EA Calc. for $C_{10}H_{17}N_2O_4Re$ (415.46): C: 28.91; H: 4.12; N: 6.74; Re: 44.82; Found: C: 29.34; H: 3.85; N: 6.79; Re: 45.19.

4.3.2. Compound **3a**

^{1}H NMR ($CDCl_3$, RT, ppm): 7.60 (N–C*H*–CH, b, 1H); 7.25–7.44 (C_6H_5, m, 5H); 6.68 (N–CH–C*H*, d, 1H); 5.99/6.22 (C(O)–N–C*H*– (*cis–trans*), m, 1H); 2.86/2.98 (N–CH_3 (*cis–trans*), m, 3H); 2.18 (Re–CH_3, s, 3H), 1.60 (CH_3, d, 3H); IR (KBr, *v*, cm^{-1}): 3168 w, 3023, w, 2980 m, 2968 m, 2942 m, 1598 st, 1528 m, 1492 m, 979 st, 943 vst (Re=O), 764 w; EA Calc. for $C_{14}H_{18}N_3O_4Re$ (478.52): C: 35.14; H: 3.79; N: 8.78; Re: 38.91; Found: C: 35.44; H: 3.72; N: 8.67; Re: 38.19.

4.3.3. Compound **5a**

^{1}H NMR (CD_2Cl_2, RT, ppm): 7.42 (N–C*H*, b, 1H); 2.90 (C–*H*, d, 1H); 2.16 (Re–CH_3, s, 3H), 2.08 (C*H*(H), m, 1H); 1.89 (C(H)*H*, m, 1H), 1.30 (CH_3, s, 3H); 1.21 (CH_2, m, 2H); 0.94 (CH_3, s, 3H), 0.71 (CH_3, s, 3H); IR (KBr, *v*, cm^{-1}): 3144 w, 3064 vw, 2984 w, 2952 m, 2912 st, 2808 m, 1577 m, 1480 m, 985 m, 942 st (Re=O); EA Calc. for $C_{12}H_{19}N_2O_3Re$ (425.50): C: 33.87; H: 4.50; N: 6.58; Re: 43.76; Found: C: 33.27; H: 4.30; N: 6.21; Re: 44.02.

4.4. Catalytic epoxidation of cis-methylstyrene with MTO and a chiral N-base auxiliary and H_2O_2 as oxidizing agent

Five milligramme (0.02 mmol) MTO is dissolved in 1 ml CH_2Cl_2 and 0.4 ml of H_2O_2 (35% in water) are added under vigorous stirring. After this the reaction solution is brought to −30 °C. After reaching this temperature 12 mol% of the chiral ligand are added and the reaction is started by further addition of *cis*-β-methylstyrene (2 mmol). The temperature in the reaction vessel is maintained via a cryostat. The course of the reaction was monitored by quantitative GC-analysis. Samples were taken after 5 and 10 min and then every 30 min diluted with 2 ml of methylene chloride and chilled in an ice bath. For the destruction of hydro peroxide and removal of water a catalytic amount of manganese dioxide and magnesium sulphate was added. After the gas evolution ceased the resulting slurry was filtered over a filter equipped Pasteur pipette and the filtrate injected in the GC column.

The conversion of the substrates as well as the formation of the epoxides was calculated from calibration curves ($r^2 = 0.999$) recorded prior to the reaction course. Blank tests without catalyst lead to no epoxide formation, tests without chiral auxiliaries led to no detectable enantiomeric excess. The method allows to determine the enantiomeric excess with an error range of below 2% (absolute).

4.5. Synthesis of MTO derived glycolates

Two hundred and fifty milligramme (1 mmol) of MTO is dissolved in 10 ml CH_2Cl_2 and 1.1 mmol of the respective diol is added under vigorous stirring. In order to remove the water formed during the course of the reaction and to shift the equilibrium on the side of the products some pellet of molecular sieves are added. The reaction mixture is refluxed for 3–4 h. During this time it turns from colorless to orange. The reaction mixture is additionally stirred at room temperature for 8–12 h. The reaction mixture is then filtered through a canula equipped with a Whatman filter and the solvent (of the filtrate) is removed in oil pump vacuum. The resulting orange–brown oil is either sublimed (in the case of the derivatives with low molecular mass) or column chromatography (pentane as eluent) is applied (heavier derivatives). In the case of the column chromatography the pentane is removed from the resulting orange solution in oil pump vacuum. The Re complexes are received as orange–brown oils or solids in yields between 50% and 95%. The elemental analyses are in accord with the expectancies according to (see Eq. (1)) in all cases. Experimental data for three selected compounds are given below.

4.6. Characterization of compounds **6a**, **8a**, and **13a** (reaction products (Re(VII)-glycolates) of the ligands **6**, **8**, and **13** with MTO)

4.6.1. Compound **6a**

^{1}H NMR (CD_2Cl_2, RT, ppm): 4.84 (O–C(COOH)–*H*, d, 2H); 2.59 (Re–CH_3, s, 3H); IR (KBr, *v*, cm^{-1}); 2985 (Re–CH_3, m); 1743 m (COO), 1360 st, 998 st, 954 vst (Re=O), 890 sh, 739 m; EA Calc. for $C_5H_7O_8Re$ (381.31): C: 15.75; H: 1.85; Re: 48.83; Found: C: 16.02; H: 2.00; Re: 48.49.

4.6.2. Compound **8a**

^{1}H NMR (CD_2Cl_2, RT, ppm): 4.50 (O–C((COEt)*H*, d, 2H); 4.30 (C–CH_2–CH_3, m, 4H); 2.57 (Re–CH_3, s, 3H); 1.30 (C–CH_2–CH_3, t, 6H); IR (KBr, *v*, cm^{-1}): 2983 st, 1744 vst, 1262 st, 1092 st, 965 st (Re=O); 863 st, 803 st, 709 m; EA Calc. for $C_9H_{15}O_8Re$ (437.42): C: 24.71; H: 3,46; Re: 42.57; Found: C: 24.89; H: 3.57; Re: 42.35.

4.6.3. Compound **13a**

^{1}H NMR (CD_2Cl_2, RT, ppm): 4.00 (C–$\underline{H}$, s, 2H); 3.80, 3.68 (O–C$\underline{H_2}$–C, dd, 4H); 2.59 (Re–C$\underline{H_3}$, s, 3H); 1.41 (s, C(C$\underline{H_3}$)$_2$, 6H); IR (KBr, ν, cm^{-1}): 2989 m, 2961 m, 2896 m, 1464 m, 1385 st, 1261 st, 1214 m, 1082 vst, 1029 vst, 984 vst 944 vst (Re=O), 892 m, 807 st, 621 m, 539 m; EA Calc. for $C_8H_{15}O_6Re$ (393.41): C: 24.42; H: 3.84; Re: 47.33; Found: C: 24.81; H: 3.89; Re: 47.02.

4.7. Catalytic epoxidation of cis-methylstyrene with MTO and a chiral diol auxiliary and H_2O_2 as oxidizing agent

Two hundred milligramme (1.69 mmol) *cis*-β-methylstyrene is added together with 2 mg (0.5 mol%) MTO, 203 μmol (12 mol%) chiral ligand, 0.65 ml methylene chloride and 0.54 ml (1.5 equiv.) H_2O_2 (30%) in a precooled (−20 to 30 °C) reaction vessel. The temperature in the reaction vessel is maintained via a cryostat. The course of the reaction was monitored by quantitative GC-analysis. Samples were taken after 5 and 10 min and then every 30 min diluted with chloroform and chilled in an ice bath. For the destruction of hydroperoxide and removal of water a catalytic amount of manganese dioxide and magnesium sulphate was added. After the gas evolution ceased the resulting slurry was filtered over a filter equipped Pasteur pipette and the filtrate injected in the GC column.

The conversion of the substrates as well as the formation of the epoxides was calculated from calibration curves ($r^2 = 0.999$) recorded prior to the reaction course. Blank tests without catalyst lead to no epoxide formation, tests without chiral auxiliaries led to no detectable enantiomeric excess. The method allows to determine the enantiomeric excess with an error range of below 2% (absolute).

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References

[1] R.A. Sheldon, second ed., in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 1, Wiley-VCH, Weinheim, 2002, pp. 412–426.
[2] H.B. Kagan, H. Mimoun, C. Marc, V. Schurig, Angew. Chem., Int. Ed. Engl 18 (1979) 485.
[3] T. Katsuki, K.B. Sharpless, J. Am. Chem. Soc. 102 (1980) 5974.
[4] I.D. Williams, S.F. Pedersen, K.B. Sharpless, S.J. Lippard, J. Am. Chem. Soc. 104 (1984) 6430.
[5] M. Palucki, P.J. Pospisil, W. Zhang, E.N. Jacobsen, J. Am. Chem. Soc. 116 (1994) 9333.
[6] P. Pietikäinen, Tetrahedron 54 (1998) 4319.
[7] S. Bellemin-Laponnaz, K.S. Coleman, J.A. Osborn, Polyhedron 18 (1999) 2533.
[8] R.J. Cross, P.D. Newman, R.D. Peacock, D. Stirling, J. Mol. Catal. A: Chem. 144 (1999) 2533.
[9] W.A. Herrmann, J.J. Haider, J. Fridgen, G.M. Lobmaier, M. Spiegler, J. Organomet. Chem. 603 (2000) 69.
[10] F.E. Kühn, A.M. Santos, A.D. Lopes, I.S. Gonçalves, J.E. Rodríguez-Borges, M. Pillinger, C.C. Romão, J. Organomet. Chem. 61 (2001) 207.
[11] I.S. Gonçalves, A.M. Santos, C.C. Romão, A.D. Lopes, J.E. Rodríguez-Borges, M. Pillinger, P. Ferreira, J. Rocha, F.E. Kühn, J. Organomet. Chem. 626 (2001) 1.
[12] J. Zhao, X. Zhou, A.M. Santos, E. Herdtweck, C.C. Romão, F.E. Kühn, J. Chem. Soc., Dalton Trans. (2003) 3786.
[13] W.A. Herrmann, F.E. Kühn, Acc. Chem. Res. 30 (1997) 169.
[14] C.C. Romão, F.E. Kühn, W.A. Herrmann, Chem. Rev. 97 (1997) 3197.
[15] J. Rudolph, K.L. Reddy, J.P. Chiang, K.B. Sharpless, J. Am. Chem. Soc. 119 (1997) 6189.
[16] C. Coperet, H. Adolfsson, K.B. Sharpless, Chem. Commun. (1997) 1565.
[17] W.A. Herrmann, H. Ding, R.M. Kratzer, F.E. Kühn, J.J. Haider, R.W. Fischer, J. Organomet. Chem. 549 (1997) 319.
[18] W.A. Herrmann, R.M. Kratzer, H. Ding, W.R. Thiel, H. Glas, J. Organomet. Chem. 555 (1998) 293.
[19] F.E. Kühn, A.M. Santos, P.W. Roesky, E. Herdtweck, W. Scherer, P. Gisdakis, I.V. Yudanov, C. Di Valentin, N. Rösch, Chem. Eur. J. 5 (1999) 3603.
[20] P. Ferreira, W.M. Xue, E. Bencze, E. Herdtweck, F.E. Kühn, Inorg. Chem. 40 (2001) 5834.
[21] S.M. Nabavizadeh, Inorg. Chem. 42 (2003) 4204.
[22] W.A. Herrmann, F.E. Kühn, M.R. Mattner, G.R.J. Artus, M. Geisberger, J.D.G. Correia, J. Organomet. Chem. 538 (1997) 203.
[23] M.J. Sabater, M.E. Domine, A. Corma, J. Catal. 210 (2002) 192.
[24] W.A. Herrmann, F.E. Kühn, M.U. Rauch, J.D.G. Correia, G. Artus, Inorg. Chem. 34 (1995) 2914.
[25] W.A. Herrmann, F.E. Kühn, P.W. Roesky, J. Organomet. Chem. 485 (1995) 243.
[26] Z. Zhu, J.H. Espenson, J. Org. Chem. 60 (1995) 1326.
[27] R.W. Murray, K. Iyanar, J. Chen, J.T. Wearing, J. Org. Chem. 61 (1996) 8099.
[28] H. Brunner, T. Scheck, Chem. Ber. 125 (1992) 701.
[29] M. Barz, E. Herdtweck, W.R. Thiel, Tetrahedron: Assym. 7 (1996) 1717.
[30] H. Glas, W.R. Thiel, Tetrahedron Lett. 39 (1998) 5509.
[31] P. Lidstrom, J. Tierney, B. Wathey, J. Westman, Tetrahedron 57 (2001) 9225 and references cited therein.
[32] A. Hroch, W.R. Thiel, Eur. J. Inorg. Chem. 3 (2000) 1107.
[33] W.R. Thiel, T. Priermeier, Angew. Chem., Int. Ed. Engl. 34 (1995) 1737.
[34] W.A. Herrmann, P. Watzlowik, J. Organomet. Chem. 441 (1992) 265.
[35] W.A. Herrmann, F.E. Kühn, R.W. Fischer, W.R. Thiel, C.C. Romão, Inorg. Chem. 31 (1992) 4431.
[36] W.A. Herrmann, R.M. Kratzer, R.W. Fischer, Angew. Chem., Int. Ed. Engl. 36 (1997) 2652.