deflected toward the apical boron above the basal plane. These trends can possibly be understood by considering the fact that as the charge on phosphorus increases, the 10a′ (HOMO) molecular orbital, which is phosphorus–apical boron antibonding in character, is destabilized (shown in Figure 3). The 5a″ orbital, which is phosphorus–apical boron bonding in nature, becomes stabilized and is therefore more important in determining the structure adapted. The calculated variation of the energies of the molecular orbitals in these small phosphaborane systems with changes in the (basal boron plane)–(bridgehead boron–phosphorus plane) dihedral angle clearly shows these trends.[1]

Acknowledgment. We wish to thank the National Science Foundation (Grant No. MSS-89-09793), the donors of the Petroleum Research Fund, administered by the American Chemical Society, the General Electric Co., the Rome Air Development Center (Award No. F30602-89-C-0113), IBM, and the Industrial Affiliates Program of the Center of Molecular Electronics for support of this work. We also wish to thank Mr. John A. Glass, Jr., for assistance with MNDO calculations included in this work.

Supplementary Material Available: A table of complete MNDO-calculated bond lengths, bond angles, interplane dihedral angles, energy terms, and internal charge distribution data for compounds **2a** (endo and exo), **3a** (endo and exo), **5a** (endo and exo), and **6a** (bridged and inserted) and a complete listing of compound data for previously reported small phosphaborane systems (^{11}B, ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR, mass spectroscopic, and yield data) (6 pages). Ordering information is given on any current masthead page.

Cp*MoO$_2$Cl-Catalyzed Epoxidation of Olefins by Alkyl Hydroperoxides

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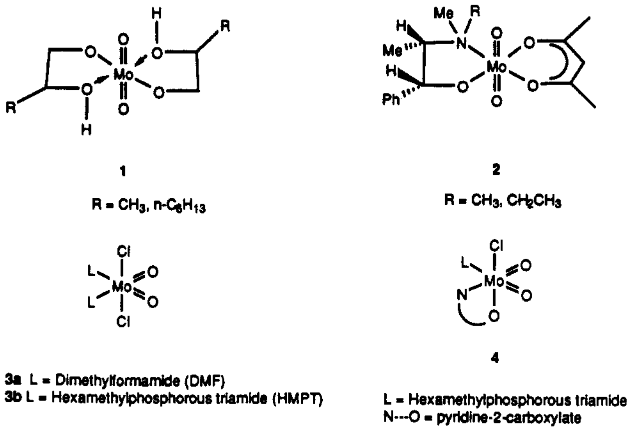
Irradiation of Cp*Mo(CO)$_3$Cl in the presence of oxygen affords the Mo^{VI} oxo complex Cp*MoO$_2$Cl (**5**). Complex **5** was found to act as a catalyst of the reaction of alkyl hydroperoxides and olefins to yield the corresponding epoxides and alcohols. No oxidation of the pentamethylcyclopentadienyl ligand of **5** was observed under the conditions of the epoxidation reaction. The characteristics of the epoxidation reaction catalyzed by **5** is similar to that of other Mo^{VI} catalysts. In the absence of added olefins, **5** reacts with alkyl hydroperoxides to yield the peroxo complex Cp*Mo(O$_2$)OCl (**6**). The peroxo complex **6** is inert to reaction with olefins, thus ruling out **6** as the intermediate responsible for olefin oxidation in this system. An investigation of the relative rate of epoxidation of cyclohexene, 1-methylcyclohexene, and 1,2-dimethylcyclohexene with various alkyl hydroperoxides demonstrates that the relative rates depend on the structure of the alkyl group of the alkyl hydroperoxide. This result demonstrates that the alkyl hydroperoxide is incorporated in the transition state for the oxygen-transfer step of the reaction.

Introduction

Molybdenum complexes are well-established catalysts for the epoxidation of olefins by alkyl hydroperoxides.[1] The usefulness and practicality of this reaction has been demonstrated by the success of the Halcon process, which is the molybdenum-catalyzed oxidation of propylene to propylene oxide by *tert*-butyl hydroperoxide.[2] Because of both the economic and scientific value of this reaction, it has been studied intensively.

Many molybdenum species are known that catalyze the epoxidation reaction, and in all cases, the active species is believed to be a Mo^{VI} compound.[1b] The coordination environment generally contains hard electronegative ligands such as oxide, carboxylate, chloride, and amide ligands, which are stable to the oxidizing conditions of the epoxidation reaction. Some problems exist in identifying the active catalyst in the epoxidation reactions. Often the original molybdenum complex is converted to its active form under the reaction conditions. This is best illustrated by Mo(CO)$_6$, which is a convenient source of molybdenum

Chart I



1

R = CH$_3$, n-C$_6$H$_{13}$

2

R = CH$_3$, CH$_2$CH$_3$

3a L = Dimethylformamide (DMF)
3b L = Hexamethylphosphorous triamide (HMPT)

4

L = Hexamethylphosphorous triamide
N---O = pyridine-2-carboxylate
or 8-hydroxyquinolinate

Scheme I

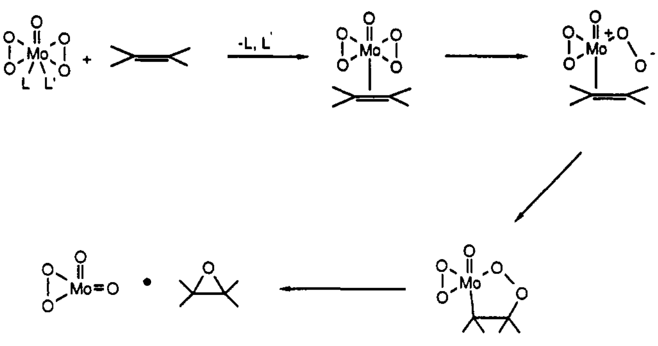
---

(1) For reviews concerning transition-metal catalysis of the epoxidation reaction, see: (a) Mimoun, H. *J. Mol. Catal.* **1980**, *7*, 1. (b) Sheldon, R. A. *J. Mol. Catal.* **1980**, *7*, 107. (c) Sharpless, K. B.; Verhoeven, T. R. *Aldrichim. Acta* **1979**, *12*, 63. (d) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981. (e) Lyons, J. E. *Aspects Homogeneous Catal.* **1977**, *3*, 1. (f) Sobczak, J.; Ziolkowski, J. J. *J. Mol. Catal.* **1981**, *13*, 11.

(2) Landau, R.; Sullivan, G. A.; Brown, D. *CHEMTECH* **1979**, 602.

0276-7333/91/2310-1172$02.50/0

Scheme II



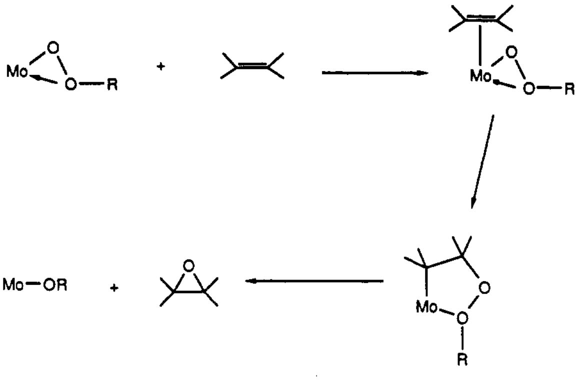
and is widely used as a catalyst.[1c,3,12a-d,15,24a] Kinetic studies have revealed the presence of an induction period prior to catalysis of the reaction, presumably due to conversion of $Mo(CO)_6$ to a catalytically active Mo^{VI} complex.[4,5] Furthermore, Sheldon has isolated the Mo^{VI} diol complex 1 (Chart I) from the $Mo(CO)_6$-catalyzed reactions. Complex 1 functions as a epoxidation catalyst without an induction period.[5] Another widely used complex is $MoO_2(acac)_2$,[4-7,12a,b] and a chiral analogue of this complex, 2, has shown some propensity to epoxidize allylic alcohols asymmetrically.[8] MoO_3 has also been used as an epoxidation catalyst, and its activity is greatly enhanced by addition of basic ligands such as HMPT.[9,10] Mimoun has reported the catalysis of the epoxidation reaction by complexes 3 and 4, which also contain basic ligands (Chart I).[11,12]

The nature of the metal species responsible for oxygen transfer to the olefin has been debated in the literature for some time. Several kinetic studies led to the proposal that the active species in the molybdenum-catalyzed reactions with a metal-coordinated alkyl hydroperoxide complex, as shown in Scheme I.[4,5,13] Sheldon and Van Doorn[13a] proposed that the main function of the metal catalyst in the coordinated hydroperoxide complex was to act as a Lewis acid and remove electron density from the peroxidic oxygen.

In 1970, Mimoun, de Roch, and Sajus reported the stoichiometric reaction between molybdenum peroxo complexes and olefins to yield epoxides.[14] This discovery led to the proposal that metal peroxo compounds could be the intermediates responsible in the catalytic reactions for oxygen transfer. The proposed mechanism of the epoxidation of olefins by peroxo complexes is shown in Scheme II.

Scheme III

Scheme IV



In 1977, Chong and Sharpless reported the results of a labeling study that cast doubt upon the proposal of peroxo intermediates and favored the intermediacy of intact alkyl hydroperoxides.[15] In this experiment, the molybdenum catalyst was treated with $H_2{}^{18}O$ to label the terminal oxo groups. Unlabeled *tert*-butyl hydroperoxide was used as the oxidant. Reaction with olefin showed no incorporation of the oxygen-18 label into the epoxide. On the basis of this result, it was concluded that the active species must be an intact alkyl hydroperoxide. This conclusion was based on the assumption that if any peroxo complex had formed, it would contain the oxygen-18 label. Two possible modes of oxygen transfer to the olefin that were proposed in this study are shown in Scheme III.

Chamumette, Mimoun, Saussine, Fischer, and Mitschler reported evidence that both peroxo and alkyl hydroperoxide intermediates were possible,[11] with the operative intermediate dependent on the alkyl hydroperoxide used. In this study, the $(DMF)_2MoO_2Cl_2$ (**3a**; see Chart I) catalyzed oxidation of *trans*-β-methylstyrene was found to give different products depending on the alkyl hydroperoxide used. When *tert*-butyl hydroperoxide was employed, the major product was the epoxide; the use of Ph_3COOH as the oxidant led to the formation of cleavage products (benzaldehyde and acetaldehyde). Because cleavage products also resulted from treatment of *trans*-β-methylstyrene with the metal peroxo complex $(DMF)_2Mo(O_2)(O)Cl_2$ (synthesized by reaction of **3a** and Ph_3COOH or H_2O_2), it was concluded that the reactions catalyzed by Ph_3COOH proceed through this peroxo intermediate while the *tert*-butyl hydroperoxide reaction must proceed via some other intermediate, presumably one containing an intact alkyl hydroperoxide. The mechanism proposed by the authors for the *tert*-butyl hydroperoxide reaction is shown in Scheme IV. Examples of vanadium[16]

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(3) For additional examples of $Mo(CO)_6$-catalyzed reactions, see: (a) Tanaku, S.; Yamamoto, H.; Nozake, H.; Sharpless, K. B.; Michaelson, R. C.; Cutting, J. D. *J. Am. Chem. Soc.* **1974**, *96*, 5254. (b) Fukuyama, T.; Vranesic, B.; Negri, D. P.; Kishi, Y. *Tetrahedron Lett.* **1978**, 2741. (c) Breslow, R.; Maresca, L. *Tetrahedron Lett.* **1977**, 628; **1978**, 887. (d) Sturtz, G.; Pondaven-Raphalen, A. *Bull. Soc. Chim. Fr.* **1983**, *5–6* (Part 2), 125. (e) Groen, M. B.; Zelen, F. J. *Tetrahedron Lett.* **1982**, *35*, 3611.

(4) Chan-Cheng, S.; Reed, J. W.; Gould, E. S. *Inorg. Chem.* **1973**, *12*, 337.

(5) Sheldon, R. A. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 253, 367.

(6) acac = acetylacetonate.

(7) Indictor, N.; Brill, W. F. *J. Org. Chem.* **1965**, *30*, 2074.

(8) Yamada, S.; Mashiko, T.; Terashima, S. *J. Am. Chem. Soc.* **1977**, *99*, 1988.

(9) HMPT = hexamethylphosphoric triamide.

(10) Yamada, S.; Mashiko, T.; Tershima, S. *J. Am. Chem. Soc.* **1977**, *99*, 1988.

(11) Chaumett, P.; Mimoun, H.; Saussine, L.; Fischer, J.; Mitschler, A. *J. Organomet. Chem.* **1983**, *250*, 291.

(12) For additional examples of molybdenum epoxidation catalysts, see: (a) Schnurpfeil, D.; Lauterbach, G.; Seyferth, K.; Taube, R. *J. Prakt. Chem.* **1984**, *326*, 1025. (b) Yamazaki, M.; Endo, H.; Tomoyama, M.; Kurusu, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3523. (c) Sobczak, J.; Ziolkowski, J. J. *J. Mol. Catal.* **1977**, *3*, 165. (d) Sobczak, J.; Ziolkowski, J. J. *J. Less-Common Met.* **1977**, *54*, 149. (e) Farberov, M. J.; Stozhkova, G. A.; Bondarenko, A. Y.; Kirik, T. M.; Ognevskaya, N. A. *Neftekhimiya* **1971**, *11*, 404.

(13) (a) Sheldon, R. A.; Van Doorn, J. A. *J. Catal.* **1973**, *31*, 427. (b) Sheng, M. N.; Zajacek, J. G. *Adv. Chem. Ser.* **1968**, *No. 76*, 418. (c) Sheng, M. N.; Zajacek, J. G. *J. Org. Chem.* **1970**, *35*, 1839. (d) Baker, T. N.; Mains, G. J.; Sheng, M. N.; Zajacek, J. G. *J. Org. Chem.* **1973**, *38*, 1145. (e) Howe, G. R.; Hiatt, R. R. *J. Org. Chem.* **1971**, *36*, 2493. (f) Sobczak, J.; Ziolkowski, J. J. *Inorg. Chim. Acta* **1976**, *19*, 15.

(14) Mimoun, H.; de Roch, S. I.; Sajus, L. *Tetrahedron* **1970**, *26*, 37.

(15) Chong, A. O.; Sharpless, K. B. *J. Org. Chem.* **1977**, *42*, 1587.

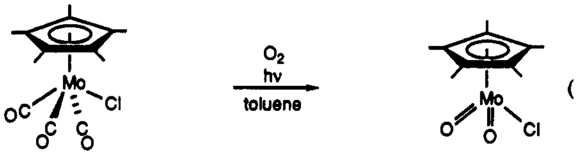
(16) (a) Mimoun, H.; Mignard, M.; Brechot, P.; Saussine, L. *J. Am. Chem. Soc.* **1986**, *108*, 3711. (b) Mimoun, H. Presented at the 196th National Meeting of the American Chemical Society, Los Angeles, CA, Sept 1988; INOR 281.

and zirconium[17] complexes containing alkyl hydroperoxide ligands capable of oxidizing olefins to epoxides have recently been reported. The oxidizing ability of these complexes affords additional evidence that alkyl hydroperoxide complexes are plausible intermediates in the catalytic systems.

In this paper, we report a modified synthesis of the organometallic Mo^{VI} oxo complex Cp*MoO$_2$Cl (5). We have found that 5 will catalyze the olefin epoxidation reaction but that the corresponding peroxo compound Cp*Mo(O$_2$)(O)Cl (6) can be generated by treatment of 5 with alkyl hydroperoxides and is inert to reaction with olefins. The catalysis of the epoxidation reaction by 5 is noteworthy both because its ligand environment is very different from that found in most molybdenum catalysts and also because the intermediacy of peroxo intermediates in the epoxidation reaction can be easily ruled out in this system. An investigation of the scope of epoxidation reactions catalyzed by 5 with particular attention to the role of the alkyl hydroperoxide is reported.

Results

Synthesis of Cp*MoO$_2$Cl. The irradiation of metal carbonyl compounds under oxygen is an increasingly reported method for the preparation of metal oxo compounds.[18] In 1964, Cousins and Green reported the synthesis of CpMoO$_2$Cl in 25% yield by the light-induced oxidation of [CpMo(CO)$_3$]$_2$ in CHCl$_3$.[19] We found that the pentamethylcyclopentadienyl analogue of this compound, Cp*MoO$_2$Cl, could be prepared in a similar fashion.[20] We chose to use the chloride complex Cp*Mo(CO)$_3$Cl as the precursor to the oxo compound rather than the dimer, as it eliminated the need to conduct the reaction in chlorinated solvents. Irradiation of Cp*Mo(CO)$_3$Cl in toluene under an oxygen purge for 2 h resulted in the formation of Cp*MoO$_2$Cl (5; eq 1). This reaction also generates some insoluble blue materials,[21] from which the desired oxo complex 5 could be separated by a toluene extraction. Following recrystallization from toluene/hexane, 5 was isolated in 61% yield. Compound 5 is air-stable in the solid state, but solutions of 5 were found to gradually decompose to insoluble blue materials upon exposure to the atmosphere. 5 is soluble in ethereal and aromatic solvents but has low solubility in saturated hydrocarbons.

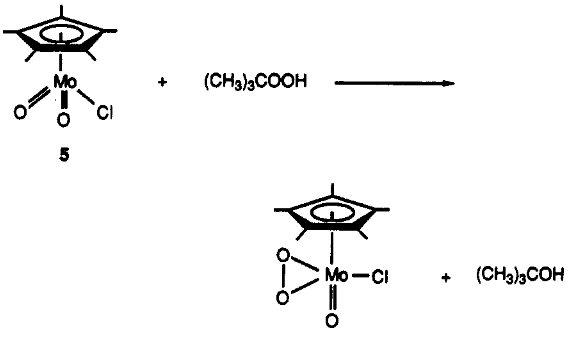


(1)

5

Elemental analysis and spectrometric methods were used to characterize complex 5. The infrared spectrum of 5 in benzene contains two intense bands at 920 and 890 cm^{-1}, values typical of terminal oxo ligands.[22] Compound 5 is yellow, its UV–vis spectrum exhibiting λ_{max} at 372 nm, with an extinction coefficient of 1.8×10^3 (cm·M)$^{-1}$. The ^{1}H NMR spectrum of 5 exhibits the expected single resonance due to the pentamethylcyclopentadienyl ligand at 1.63 ppm in benzene-d_6. The presence of the chloride ligand was confirmed by elemental analysis, which assayed for the correct amount of chlorine.

Reaction of 5 with Alkyl Hydroperoxides. Heating a solution of 5 with 12 equiv of *tert*-butyl hydroperoxide at 45 °C for 4 h led to production of the peroxo complex 6 in 71% isolated yield, along with *tert*-butyl alcohol (eq 2).[23] We found that other alkyl hydroperoxides such as cumene hydroperoxide and Ph$_3$COOH as well as hydrogen peroxide would also react with 5 to yield the peroxo complex 6. The only alkyl hydroperoxide tried that failed to convert 5 to the peroxo complex was *n*-hexyl hydroperoxide; rather, this led to slow decomposition of 5 to insoluble white materials and the conversion of *n*-hexyl hydroperoxide to *n*-hexyl alcohol. Peroxo complex 6 is more sensitive than the coresponding oxo compound 5. In the solid state, 6 decomposed explosively when heated to 74 °C in a glass capillary sealed under nitrogen. It is also shock-sensitive; in two instances, we found that scraping solid 6 with a metal spatula under a nitrogen atmosphere led to a mild explosion and complete decomposition of 6 (see Experimental Section).



5

6

(2)

Compound 6 was characterized by elemental analysis and spectrometric methods. The infrared spectrum exhibited two intense bands at 934 and 884 cm^{-1} and weaker bands at 571 and 543 cm^{-1} (KBr pellet). By comparison of these values to those observed in other molybdenum oxo and peroxo compounds, the 934-μm^{-1} band can be assigned as a terminal metal–oxo stretch, the 884-cm^{-1} band as an oxygen–oxygen stretch of the peroxo group, and the 571- and 543-cm^{-1} bands as the metal–oxygen stretch of the peroxo moiety.[11,23] The UV–vis spectrum of 6 exhibits λ_{max} at a wavelength slightly shorter (328 nm, $\epsilon = 1.9 \times 10^3$ (cm·M)$^{-1}$) than that observed with the oxo compound 5. The resonance due to the pentamethylcyclopentadienyl ligand in the ^{1}H NMR spectrum (benzene-d_6) appears at 1.53 ppm, a value slightly upfield from that observed in

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[17] Lubben, T. V.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1985**, *107*, 701.

[18] For examples of the use of this reaction to synthesize metal oxo complexes, see: (a) Bokiy, N. G.; Garilow, Y. V.; Struchkov, Y. T.; Ustynyuk, N. A. *J. Organomet. Chem.* **1973**, *213*, 54. (b) Herrmann, W. A.; Serrano, R.; Schafer, A.; Kusthardt, U.; Ziegler, M. L.; Guggolz, E. *J. Organomet. Chem.* **1984**, *272*, 55. (c) Klahn-Oliva, A. H.; Sutton, D. *Organometallics* **1984**, *3*, 1313. (d) Hermann, W. A.; Serrano, R.; Bock, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 383. (e) Herberhold, M.; Kremnitz, W.; Razavi, A.; Schollhorn, H.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 601. (f) Herrmann, W. A.; Voss, E.; Floel, M. *J. Organomet. Chem.* **1985**, *297*, C5. (g) Burkhardt, E. R.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2022.

[19] Cousins, M.; Green, M. L. H. *J. Chem. Soc.* **1964**, 1567.

[20] The synthesis of 5 by reaction of (Cp*MoO$_2$)$_2$O and PCl$_5$ has recently been reported. See: (a) Faller, J. W.; Ma, Y. *J. Organomet. Chem.* **1988**, *340*, 59. (b) Faller, J. W.; Ma, Y. *J. Organomet. Chem.* **1989**, *368*, 45.

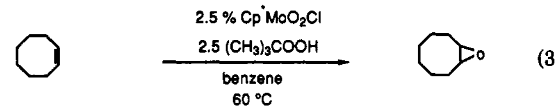
[21] The identities of the blue solids are likely mixed oxides of Mo^{VI} and Mo^{V}, which are generally referred to as molybdenum blue. See: Cotton, F. A.; Wilkinson, G. *Comprehensive Inorganic Chemistry*; Wiley: New York, 1980; p 848.

[22] Griffith, W. P. *Coord. Chem. Rev.* **1970**, *5*, 459.

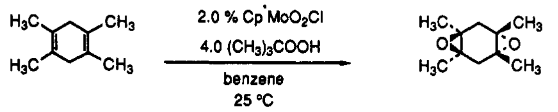
[23] Similar methods for the synthesis of this and several related molybdenum and tungsten peroxo complexes have recently been reported. See: (a) Reference 20b. (b) Faller, J. W.; Ma, Y. *Organometallics* **1988**, *7*, 559. (c) Legzdins, P.; Phillips, E. C.; Rettig, S. J.; Sanchez, L.; Trotter, J.; Yee, V. C. *Organometallics* **1988**, *7*, 1877. (d) Legzdins, P.; Phillips, E. C.; Sanchez, L. *Organometallics* **1989**, *8*, 940.

5. The presence of the chloride ligand was confirmed by elemental analysis.

Epoxidation of Olefins Catalyzed by 5. In the presence of an appropriate olefin and *tert*-butyl hydroperoxide, **5** will function as an olefin epoxidation catalyst. When the epoxidation reactions are conducted in a deuterated solvent and in progress is monitored by ^{1}H NMR spectroscopy, it can be observed that complex **5** maintains its integrity during the reaction (except for some formation of peroxo complex **6**, vide infra) with no observable oxidation of the pentamethylcyclopentadienyl ligand. The epoxidation reaction occurs under quite mild conditions. Cyclooctene was converted to cyclooctene oxide in 80% isolated yield with use of 2.5 mol % of **5** and 2.5 equiv of *tert*-butyl hydroperoxide in benzene solution after 4 h at 60 °C (eq 3). The tetrasubstituted olefin 1,2,4,5-tetramethylcyclohexa-1,4-diene was converted to the diepoxide **7** (eq 4) in 72% isolated yield with use of 2% of the catalyst **5** and 4 equiv of *tert*-butyl hydroperoxide (2 equiv per double bond). This reaction proceeded at room temperature, although the exothermicity of the reaction caused a rise in temperature of the reaction mixture. As seen in other transition-metal-mediated epoxidation reactions, geraniol was epoxidized selectively at the olefin bearing the allylic hydroxyl group, affording **8** in 27% isolated yield (eq 5).[24] The epoxidation of β-methylstyrene (2.5% of **5**, 2.5 equiv of *tert*-butyl hydroperoxide) was monitored by both ^{1}H NMR spectrometry and gas chromatography. Only production of the epoxide was observed (92% yield by gas chromatography) with no evidence for cleavage products.

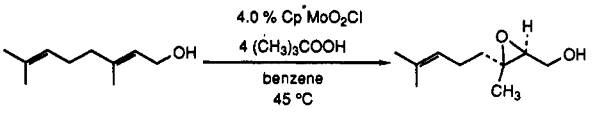


(3)



(4)

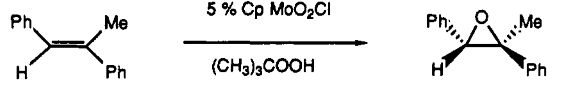
7



(5)

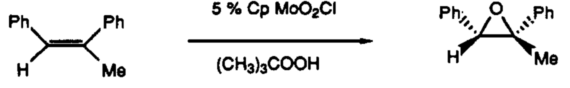
8

The epoxidation reaction is stereoselective. Epoxidation of *trans*-1,2-diphenylpropene led only to the trans epoxide **9** (eq 6), while epoxidation of *cis*-1,2-diphenylpropene under similar conditions gave exclusively the cis epoxide **10** (eq 7). No epoxidation was observed for the reaction catalyzed by **5** and olefins containing electron-withdrawing substituents. Allyl chloride and α,β-unsaturated ketones failed to yield the corresponding epoxides when treated with **5** and *tert*-butyl hydroperoxide.



(6)

9



(7)

10

Other alkyl hydroperoxides that were found to function as oxidants in the epoxidation reaction are cumene hydroperoxide, 3-ethyl-3-hexyl hydroperoxide, and *n*-hexyl hydroperoxide. In contrast, both hydrogen peroxide and Ph$_3$COOH failed to give any epoxide when reacted with **5** and an olefin; only conversion of **5** to **6** was observed.

Reactivity of the Peroxo Complex 6 toward Olefins. The peroxo complex **6** does not react with olefins to yield epoxides. Treatment of **6** with very reactive olefins such as 1-methylcyclohexene failed to give any detectable reaction, even in the presence of added *tert*-butyl hydroperoxide. In attempts to catalytically epoxidize slowly reacting olefins (e.g. *trans*-stilbene) with **5**, the production of **6** was detected and its complete formation shuts down the reaction. Thus, **6** is a poisoned form of the catalyst in this system, and its formation is a side reaction that limits the usefulness of **5** as an epoxidation catalyst.

Dependence of the Relative Rates of Epoxidation of Olefins upon the Nature of the Alkyl Hydroperoxide. Electron-rich olefins react most rapidly in the epoxidation reaction catalyzed by **5**. This was demonstrated by using competition studies to determine the relative rates of reaction of cyclohexene, 1-methylcyclohexene, and 1,2-dimethylcyclohexene. These olefins could be converted to the corresponding epoxides in at least 85% yield (see Experimental Section). The relative rates were measured by using mixtures of two olefins, approximately 10% of **5**, and a limiting amount of *tert*-butyl hydroperoxide. At least 10 equiv of each olefin was used relative to the *tert*-butyl hydroperoxide to ensure that the concentration of olefin did not change appreciably during the reaction. The reaction mixtures were analyzed by gas chromatography. With *tert*-butyl hydroperoxide as an oxidant, the rate constant ratio for epoxidation of cyclohexene/1-methylcyclohexene/1,2-dimethylcyclohexene was 1.0/5.8/14. Significantly (see Discussion), these relative rates were dependent on the alkyl hydroperoxide used. Thus, with *n*-hexyl hydroperoxide the ratio changed to 1.0/6.9/21, and with 3-ethyl-3-hexyl hydroperoxide this ratio was 1.0/4.9/9.3. Monitoring and repetition experiments demonstrated that the epoxides were stable to the reaction conditions and the ratios were reproducible to ±5%.

Discussion

Epoxidation of Olefins Catalyzed by 5. The characteristics of the epoxidation reactions catalyzed by **5** are similar to those of other known molybdenum systems.[1b] The reaction is electrophilic in nature and so more electron-rich olefins react faster. Allylic alcohols are epoxidized in preference to isolated double bonds. The reaction is stereospecific, with the stereochemistry of double bonds remaining unchanged after epoxidation.

The lack of reactivity of the peroxo complex **6** demonstrates that in this system it cannot be the intermediate responsible for oxygen transfer. The absence of an epoxidation reaction when Ph$_3$COOH and H$_2$O$_2$ are used as oxidants must be due to the formation of **6** in preference to the epoxidation reaction.[25]

Because the intermediacy of a peroxo complex could be ruled out in the epoxidation reactions catalyzed by **5**, we

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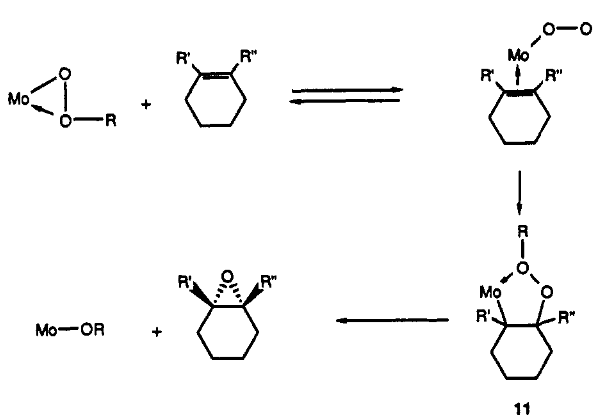
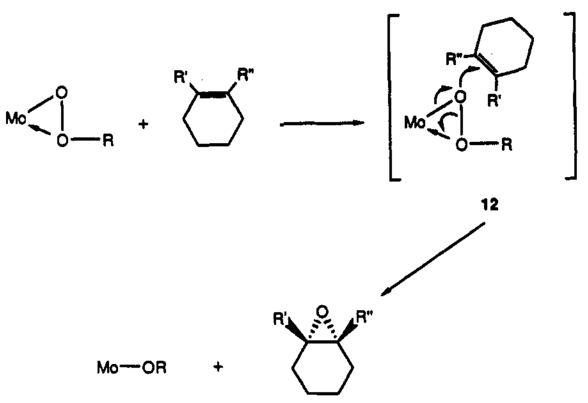
(24) (a) Sharpless, K. B.; Michaelson, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6136. (b) Trost, B. M.; Masuyama, Y. *Isr. J. Chem.* **1984**, *24*, 134.

(25) Mimoun has attributed the lack of reactivity of some peroxo complexes to the lack of an available coordination site on the metal for the olefin to bind prior to reaction. See: Mimoun, H. *Isr. J. Chem.* **1983**, *23*, 451.

Scheme V



Scheme VI



felt that this system was particularly well suited to a study of the effect of the alkyl hydroperoxide on the reaction. We chose to focus on the study of the relative rate of epoxidation. Kinetic studies of the Mo epoxidation reaction have led to the proposal that the alkyl hydroperoxide first reacts with the metal species and then the olefin reacts with this intermediate in a second step.[4,5,12] Allowing a mixture of olefins to compete for the intermediate should provide information on the dependence of the intermediate's selectivity on the alkyl hydroperoxide used.

As described in the Results, the ratio of relative rates depended on the alkyl hydroperoxide used. The difference in relative rates between these three olefins was greatest when *n*-hexyl hydroperoxide was used and smallest with 3-ethyl-3-hexyl hydroperoxide. These results demonstrate that the alkyl group of the alkyl hydroperoxide moiety must be associated with the species responsible for the oxygen transfer. The difference in relative rates between the alkyl hydroperoxides appears to be caused by a steric effect. The more sterically demanding 3-ethyl-3-hexyl hydroperoxide retards the relative rate of epoxidation of the more highly substituted olefins, while the less bulky *n*-hexyl hydroperoxide increases their susceptibility to epoxidation.

If the differences in relative rates are due to a steric effect, then there must be some point in the mechanism of the epoxidation reaction in which substantial steric interactions between the hydroperoxide alkyl group and the olefin occur, resulting in the observed variation of the rates. Two mechanistic explanations will be discussed. The first is based upon the mechanism proposed by Mimoun for the stoichiometric epoxidation of olefins by vanadium alkyl hydroperoxide complexes (Scheme V).[16] This mechanism proceeds by an initial reversible binding of the olefin to the metal center followed by attack of the metal-bound alkyl hydroperoxide on the olefin. The cyclic intermediate 11 then breaks down to epoxide and a metal alkoxide. The differences in rate could be caused by a lowered binding affinity of the more substituted olefins to the metal center because of steric interactions with the hydroperoxide alkyl group.[26] Steric interactions between the alkyl group of the hydroperoxide and the olefin could also affect the rate of the second step, formation of the cyclic intermediate 11. Since the second step is believed to be irreversible, subsequent steps should not affect the relative rates. Another mechanism consistent with the experimental results is a direct attack on the olefin by the alkyl hydroperoxide oxygen, as proposed by Sharpless (Scheme VI).[15] In this case, steric interactions between the more substituted olefin and the hydroperoxide alkyl group in the transition state 12 would account for the observed rate differences. On the basis of the results of this study, we cannot differentiate between these two mechanisms, as they both contain elements that could account for the observed steric effect.

Conclusion

We have shown that Cp*MoO_2Cl will act as a catalyst for the epoxidation of olefins by alkyl hydroperoxides. The catalytic properties of 5 are similar to those of other Mo catalysts, even though the ligand environment of 5 is different. Investigation of the relative rate dependence upon the alkyl hydroperoxide was consistent with the formation of an intermediate species in which the alkyl group of the hydroperoxide moiety is intact. Surprisingly, the pentamethylcyclopentadienyl ligand is stable to the conditions of the epoxidation reaction and the major reaction responsible for degradation of the catalyst is the conversion of 5 to the peroxo complex 6. Many Mo^{VI} oxo complexes are epoxidation catalysts; however, the reactivity of their corresponding peroxo complexes is variable. The use of a catalyst that forms a nonreactive peroxo complex may led to a cleaner yield of epoxides with less cleavage product, although it has the disadvantage that peroxo formation poisons the active catalyst. The oxidative poisoning of molybdenum catalysts that has been observed in other systems may also be due to the formation of unreactive peroxo complexes. It is hoped the finding that 5 catalyzes the epoxidation reaction will aid in the future design of catalysts of the epoxidation reaction.

Experimental Section

General Considerations. Unless otherwise noted, all manipulations were conducted under an atmosphere of nitrogen by utilization of standard drybox, vacuum line, or Schlenk techniques. Drybox operations were conducted under a recirculating atmosphere of nitrogen maintained at a constant level of under 1 ppm of oxygen and 1 ppm of H_2O in a Vacuum Atmospheres HE-533 Dri-Lab with an attached MO-40 Dri-Train. The amount of oxygen in the drybox atmosphere were constantly monitored by a Teledyne Model No. 316 trace oxygen analyzer, and the H_2O level in the atmosphere was monitored by a E & H Ondyne Model No. 1400 hygrometer. The drybox was equipped with a −40 °C freezer.

Proton NMR spectra were recorded on either a commercial Bruker AM-500 instrument or a 300-MHz instrument assembled by Mr. Rudi Nunlist of the University of California, Berkeley, NMR facility. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane. Chemical shifts of ^1H NMR spectra were recorded relative to residual protiated solvent: benzene-d_6, 7.15 ppm. Carbon-13 spectra were obtained at either 75.5 or 125.7 MHz, and chemical shifts are reported relative to

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[26] This argument has been used by Mimoun to explain differences in rates between olefins in competition versus the rates observed with a single olefin.[16]

the solvent resonance: benzene-d_6, 128.0 ppm. Multiplicities are assigned as follows: s, singlet; d, doublet, t, triplet, m, multiplet. Coupling constants are reported in hertz.

Infrared (IR) spectra were recorded on a Perkin-Elmer Model 1550 Fourier transform spectrometer equipped with a Model 7500 computer. Samples were prepared in the drybox with use of 0.025 mm path length potassium bromide solution cells.

"Bombs" refer to cylindrical Pyrex vessels fused to Kontes Model No. K-826500 Teflon high-vacuum valves. Melting points were recorded in sealed capillary tubes on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Mass spectra were obtained at the University of California, Berkeley (UCB) mass spectrometry facility on AEI MS-12 or Finnigan 4000 mass spectrometers. Elemental analyses were performed by the UCB microanalytical laboratory. Preparative flash chromatography was performed on Merck 230–400-mesh silica gel. Gas chromatographic analyses were performed with a Hewlett-Packard Model 5840A gas chromatograph interfaced with a Hewlett-Packard Model 3393A electronic integrator employing a J and W Scientific fused silica capillary column with a DB-5 liquid phase. All photolyses were carried out at 5–10 °C. The photolysis apparatus consisted of a 450-W medium-pressure Conrad-Hanovia mercury immersion lamp in an Ace 7874B-38 immersion well. The immersion well was secured in a stainless steel beaker filled with water cooled by a Forma Scientific Model 2095 refrigerated bath circulator.

Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. Hexane was distilled from $LiAlH_4$ under nitrogen. Benzene, toluene, and diethyl ether were dried over sodium benzophenone ketyl under nitrogen. Benzene-d_6 was distilled from sodium–benzophenone ketyl and was stored under vacuum. Cyclohexene, 1-methylcyclohexene, and 1,2-dimethylcyclohexene were distilled from CaH_2. Geraniol and cyclooctene were distilled prior to use. Solutions of anhydrous *tert*-butyl hydroperoxides were prepared as described by Sharpless et al.[27] or were purchased from Aldrich as 3 M solutions in 2,2,4-trimethylpentane. Cp*Mo(CO)$_3$Cl was prepared by treatment of Cp*Mo(CO)$_3$H[28] with carbon tetrachloride. The peroxides 3-ethyl-3-hexyl hydroperoxide[29] and *n*-hexyl hydroperoxide[30] were prepared by literature methods.

Cp*MoO$_2$Cl (5). In the drybox, a 100-mL bomb was charged with a solution of 0.980 g (2.79 mmol) of Cp*Mo(CO)$_3$Cl in 50 mL of toluene. Oxygen was bubbled through the solution via a 24-gauge syringe needle at a rate of approximately 2 bubbles/s while the solution was irradiated at 5 °C. The reaction was monitored by IR spectrometry and was stopped after 90 min when the absorbances due to the carbonyl ligands of the starting material at 1700–2000 cm^{-1} had disappeared. During the reaction, the solution turned from a red-orange to an amber shade with some blue solids precipitated on the sides of the reaction vessel. The toluene was removed under vacuum, leaving a brown solid. The solid was taken up in toluene in the drybox and the resulting solution filtered through a medium-porosity sintered-glass frit to remove insoluble blue impurities. Recrystallization from toluene/hexane afforded 0.508 g (1.70 mmol, 61% yield) of 5 as a yellow solid: mp 151–157 °C dec; ^{1}H NMR (C_6D_6) δ 1.63 (s); ^{13}C{^{1}H} NMR (C_6D_6) δ 122.3, 11.1; IR (C_6D_6) 920 (s), 890 (s) cm^{-1}; UV–vis (toluene) λ_{max} = 372 nm, ϵ = 1.8 × 10^3 (M·cm)$^{-1}$. Anal. Calcd for $C_{10}H_{15}O_2ClMo$: C, 40.22; H, 5.06; Cl, 11.87. Found: C, 40.09; H, 5.05; Cl, 11.78.

Preparation of Cp*Mo(O$_2$)OCl (6). In the drybox, a 10-mL bomb was charged with 0.120 g (0.402 mmol) of 5 and 3 mL of toluene. Anhydrous *tert*-butyl hydroperoxide in toluene (2.6 M, 1.85 mL, 4.82 mmol) was added via syringe. The bomb was heated to 45 °C for 4 h. A slight change in color to a paler shade of yellow was noted. The toluene and the excess *tert*-butyl hydroperoxide were removed under vacuum, leaving a pale yellow solid. Recrystallization from toluene/hexane at −40 °C yielded 0.090 (0.286 mmol, 71% yield) of 6 as yellow needles, mp 74–77 °C (decomposed explosively). *Warning! Complex 6 is potentially explosive and can be set off either by heat or by mechanical shock. We do not recommend preparing quantities larger than 0.100 g.* ^{1}H NMR (C_6D_6): δ 1.53 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 125.2, 10.4. IR (KBr): 934 (s), 884 (s), 571 (m), 543 (m) cm^{-1}. UV–vis: λ_{max} = 328 nM, ϵ = 1.9 × 10^3 (M·cm)$^{-1}$. Anal. Calcd for $C_{10}H_{15}O_2ClMo$: C, 38.18; H, 4.81; Cl, 11.27. Found: C, 37.85; H, 4.70; Cl, 10.84.

Epoxidation of Cyclooctene. In the drybox, a solution of 5 (0.101 g, 0.338 mmol) in 5 mL of benzene was placed into a 50-mL bomb. Cyclooctene (1.77 mL, 13.58 mmol) was added via syringe. Outside the drybox, 11.32 mL (33.97 mmol) of a 3 M *tert*-butyl hydroperoxide solution in 2,2,4-trimethylpentane was added. The bomb was heated to 60 °C for 3 h. The solution was then diluted to a total volume of 150 mL with benzene. The organic layer was washed six times with 100 mL of water to remove excess hydroperoxide and then washed with 100 mL of saturated NaCl and dried over $MgSO_4$. The benzene was removed under vacuum, and the crude product was purified by flash chromatography on silica gel, with 10% ethyl acetate/90% hexane as eluent, to yield 1.37 g (10.8 mmol, 80% yield) of cyclooctene oxide, >95% pure by ^{1}H NMR spectroscopy. The epoxide was identified by comparison of its proton NMR spectrum and GC retention time with those of an authentic sample.

Epoxidation of 1,2,4,5-Tetramethylcyclohexadiene. A solution of 0.068 g (0.229 mmol) of 5 in 7 mL of benzene was placed into a 50-mL bomb. The diene 1,2,4,5-tetramethylcyclohexadiene (1.56 g, 11.45 mmol) and 15.3 mL (45.8 mmol) of a 3 M solution of *tert*-butyl hydroperoxide in 2,2,4-trimethylpentane were added. Upon addition of the peroxide, the solution became noticeably warm and the solution was left to react at room temperature for 3 h. Workup consisted of dilution to a total volume of 150 mL with benzene, six washes of the organic layer with 100 mL of water, one wash with 100 mL of saturated $NaHCO_3$, and one wash with 100 mL of saturated NaCl. The organic layer was dried over $MgSO_4$ and the solvent removed under vacuum to leave a yellow solid. Sublimation of the crude product at 70 °C (1 Torr) afforded 1.39 g (8.24 mmol, 72% yield) of the diepoxide 7 as a waxy white solid: mp 93–95 °C; ^{1}H NMR (C_6D_6) δ 1.94 (s, 4 H), 1.05 (s, 12 H); ^{13}C NMR (C_6D_6) δ 59.8, 38.9, 20.4; MS *m/e* 168, 43 (M$^+$, base).

Epoxidation of Geraniol. A 50-mL bomb was charged with 2.00 g (11.5 mmol) of geraniol, 0.138 g (0.46 mmol) of 5, and 4 mL of toluene. Outside the drybox, 11.53 mL (3 M, 34.58 mmol) of a solution of *tert*-butyl hydroperoxide in 2,2,4-trimethylpentane was added via syringe. The reaction mixture became warm and was left at room temperature for 1 h and then heated to 45 °C for 6 h. To monitor the progress of the reaction, small aliquots were taken, passed through a plug of silica gel to remove the molybdenum oxo complex 5, and then analyzed by GC. Workup consisted of dilution to 100 mL with toluene, followed by three washes of the organic layer with 100 mL of water and one wash with 100 mL of saturated NaCl. The organic layer was dried over $MgSO_4$, and the solvent was removed under vacuum to afford a colorless oil. Inspection of the crude reaction mixture by ^{1}H NMR spectroscopy revealed that it consisted of a small amount of starting material, some aldehyde-containing products, and mostly the epoxide 8. The epoxide was purified by flash chromatography on silica gel, with 1:4 ethyl acetate/hexane as eluent, to yield 0.562 g (3.35 mmol, 29% yield) of 8 as a clear oil. The product was identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample, prepared as described by Sharpless in ref 24a, with the exclusion of the acylation step. ^{1}H NMR (C_6D_6): δ 5.7 (t of apparent t, 1 H, *J* = 7.1, 1.4), 3.66 (t of d, 1 H, *J* = 12.1, 4.3), 3.61 (t of d, 1 H, *J* = 12.1, 6.4), 3.26 (broad s, 1 H), 2.94 (d of d, 1 H, *J* = 6.4, 4.3), 2.02 (t of d, 2 H, *J* = 7.8, 7.4), 1.62 (d, 3 H, *J* = 5.3), 1.49 (s, 3 H), 1.49 (s, 3 H), 1.4–1.6 (complex m, 2 H), 1.09 (s, 3 H).

Epoxidation of (*E*)-1,2-Diphenylpropene and (*Z*)-1,2-Diphenylpropene. In the drybox, a 10-mL bomb was charged with 0.100 g (0.514 mmol) of (*E*)-1,2-diphenylpropene, 0.008 g (0.026 mmol) of Cp*MoO$_2$Cl dissolved in 2 mL of toluene, and 0.171 mL (0.514 mmol) of a 3.0 M solution of *tert*-butyl hydroperoxide in 2,2,4-trimethylpentane. This mixture was allowed to react for 2 h at room temperature and then analyzed by gas chromatography. Only the trans epoxide 9 and starting material (approximately a 1:1 mixture) were detected by gas chromatography, with no evidence of the cis epoxidation product. In the same manner,

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the reaction was conducted for (*Z*)-1,2-diphenylpropene. In this case, only the cis epoxide **10** and starting material were detected by gas chromatographic analysis of the reaction mixture. The identities of both the trans and cis epoxides were established by comparison to authentic samples.[31]

Epoxidation of Cyclohexene, 1-Methylcyclohexene, and 1,2-Dimethylcyclohexene. Due to the volatility of these epoxides, the yields were determined by gas chromatography. These yields were determined at low conversion (10–40% reaction) to ensure that all of the peroxide had reacted (analysis of mixtures containing large amounts of hydroperoxide resulted in low yields, presumably due to decomposition upon injection into the GC). The yields are corrected for unreacted starting material. A typical procedure is described for cyclohexene. A 10-mL bomb was charged with 0.25 mL (2.47 mmol) of cyclohexene and 0.17 mL of mesitylene (0.62 mmol) as an internal standard. A drop of this mixture was removed and analyzed by gas chromatography to determine the ratio of olefin to mesitylene. To the remaining solution were added 0.018 g (0.062 mmol) of Cp*MoO$_2$Cl in 1 mL of toluene and 0.23 mL (3 M, 0.62 mmol) of *tert*-butyl hydroperoxide in toluene. The mixture was allowed to react at room temperature for 1 h. Gas chromatographic analysis of the reaction mixture revealed that 9.5% of the olefin had been converted to cyclohexene epoxide in 85% yield. In the same manner, the yield of methylcyclohexene epoxide was found to be 93% and the yield of 1,2-dimethylcyclohexene epoxide was found to be 99%. The identities of the three epoxides were determined by comparison to authentic samples.

Relative Rate Studies. In a typical procedure, a stock solution of 0.05 mL of 1,2-dimethylcyclohexene (3.70 mmol) and 1.5 mL of cyclohexene (14.8 mmol) was prepared and analyzed by gas chromatography to determine the ratio of the two olefins. The samples for the relative rate determinations were prepared by charging a 10-mL bomb with 0.50 mL of the stock solution (3.70 mmol of cyclohexene, 0.925 mmol of 1,2-dimethylcyclohexene), 0.003 g (0.010 mmol) of Cp*MoO$_2$Cl, and 0.015 mL (0.083 mmol) of 3-ethyl-3-hexyl hydroperoxide. The mixture was allowed to react for 1 h at room temperature and then analyzed by gas chromatography. The data were corrected for the relative concentrations of the olefins as well as the relative response of the flame ionization detector of the gas chromatograph. The response correction factor of the FID detector was measured by integration of the response of each analyte against an internal standard. This was calculated over a concentration regime corresponding to that used in these experiments, and the response factors were found to be nearly linearly dependent on the concentration in this range.

Similarly, the relative rates were measured with *tert*-butyl hydroperoxide (used as a 2.7 M solution in toluene) and *n*-hexyl hydroperoxide. As a check on the data obtained, the relative amount of the olefins was varied (29.62 mmol of cyclohexene and 3.7 mmol of 1,2-dimethylcyclohexene). This gave the same relative rates within 5%.

As an additional check, several runs were monitored by gas chromatography over a 4-h time span to ensure the products were stable to the reaction conditions. No significant change in the relative amounts of the two epoxides was detected in these experiments.

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Registry No. 5, 119782-31-9; **6**, 125978-97-4; **7**, 132774-70-0; **8**, 62960-04-7; **9**, 23355-99-9; **10**, 10282-18-5; Cp*Mo(CO)$_3$Cl, 63511-23-9; cyclooctene, 931-88-4; cyclooctene oxide, 286-62-4; 1,2,4,5-tetramethylcyclohexadiene, 26976-92-1; geraniol, 106-24-1; (*E*)-1,2-diphenylpropene, 833-81-8; (*Z*)-1,2-diphenylpropene, 1017-22-7; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; 1,2-dimethylcyclohexene, 1674-10-8; cyclohexene epoxide, 286-20-4; methylcyclohexene epoxide, 1713-33-3; dimethylcyclohexene epoxide, 17612-36-1; *tert*-butyl hydroperoxide, 75-91-2; 3-ethyl-3-hexyl hydroperoxide, 90951-85-2; *n*-hexyl hydroperoxide, 4312-76-9.

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(31) These epoxides were prepared by reaction of the respective olefins with *p*-chloroperbenzoic acid. For a general description of the procedure see: Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1, p 135.

Synthesis and Reactivity of α-(Dichloroorganyltelluro) Ketones

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The reaction of equimolar amounts of ketones or ketone trimethylsilylenol ethers with organyltellurium trichlorides in boiling benzene produces α-(dichloroorganyltelluro) ketones. The yields are good in the reaction of ketones and ketone silylenol ethers with (*p*-methoxyphenyl)tellurium trichloride; however, the reaction with aliphatic tellurium trichlorides gives good results only with ketone silyl enol ethers; reaction with ketones gives low yields of the α-(dichloroorganyltelluro) ketones. α-[Dichloro(*p*-methoxyphenyl)telluro]acetophenone and α-[dichloro(*p*-methoxyphenyl)telluro]pinacolone afford the corresponding α-chloro ketone in good yield on pyrolysis. Under similar conditions, the α-[dichloro(*p*-methoxyphenyl)telluro]cycloalkanones give low yields of the α-chloro ketones. Reaction of the α-(dichloroorganyltelluro) ketones with halogens (Cl$_2$, Br$_2$) gives the corresponding α-halo ketone even in the case of the cycloalkanones. The α-(dichloroorganyltelluro) ketones were characterized by ^{1}H and ^{13}C NMR and IR spectroscopies. X-ray analyses of α-[dichloro(*p*-methoxyphenyl)telluro]cyclohexanone showed that the intramolecular distance Te---O is shorter than the sum of the van der Waals radii of the Te and O, indicating an interaction between the tellurium atom and the carbonyl oxygen.

Introduction

Although α-thio- and α-selenocarbonyl compounds are well-known and are valuable synthetic tools, their tellurium counterparts have scarcely been investigated and only a few reports deal with the synthesis and reactivity of this class of organoelemental compounds.[1-13] The most complete study concerning this matter reports the synthesis

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