Convenient Synthesis of Bis(alkoxy)rhenium(VII) Complexes

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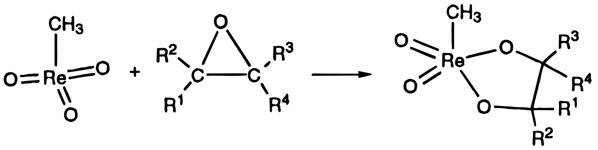
The study of high-oxidation-state organorhenium compounds has been a field of continuing activity, thanks to the success of methylrhenium trioxide (CH_3ReO_3 or MTO) in catalytic processes. This catalyst is effective in oxidations,[1−3] olefin metathesis,[4] the olefination of aldehydes,[5] and the preparation of other compounds with three-membered rings.[6] The syntheses of some rhenium compounds derived from MTO have been reported.[5] Epoxide formation is a key reaction,[7−9] and it bears directly on these findings, as we now report.

Re(VII) complexes containing a chelated bis(diolate) ligand can be synthesized by refluxing MTO with 2,3-dimethyl-2,3-diol.[10] Here we report a more convenient method for this preparation. A different series of related compounds consists of chelated bis(diolates) of the Cp*Re−oxo series, Cp*ReO(diolate).[11,12]

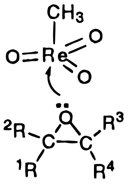
Results and Discussion

The reaction between MTO and an epoxide, eq 1, leads to diolate complexes. Five epoxides were used in this study: 2,3-dimethyl-2-butene epoxide, styrene epoxide, *cis*-cyclododecane epoxide, *cis*-stilbene oxide, and *trans*-stilbene oxide. All except the last react with methylrhenium trioxide to give the corresponding bis(alkoxy)rhenium(VII) compounds (**I**) in nearly quantitative yield.

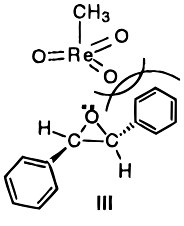


I (1)

We suggest that the first step is the approach of the oxygen atom of the epoxide to the rhenium atom, at a site remote from the Re−C bond (**II**). Unfavorable steric interactions may account for the failure of *trans*-stilbene oxide to react with MTO, since a similar approach would be impeded by the disposition of the phenyl groups (**III**).



II



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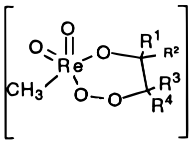
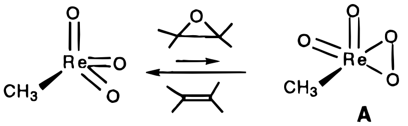


IV

The bis(alkoxy)rhenium(VII) complexes react with triphenylphosphine in dry benzene at room temperature to yield MTO, triphenylphosphine oxide, and olefin:

$$CH_3Re(O)_2(OCR_2CR_2O) + PPh_3 \rightarrow CH_3ReO_3 + Ph_3P{=}O + CR_2CR_2 \quad (2)$$

Release of an alkene is strongly enhanced by the phosphine, and it occurs essentially upon mixing. Without phosphine, alkenes are released only slowly, if at all, from these Re(VII) derivatives; if heated, the MTO is destroyed. In wet acetonitrile, the reactions of styrene epoxide and 2,3-dimethyl-2-butene epoxide with MTO also gave bis(alkoxy)rhenium(VII) complexes in the presence and in the absence of H_2O_2. The yield (∼10−15%) was much less than that obtained in dry benzene or in chloroform. In the absence of hydrogen peroxide, alkenes were released slowly over 3−5 days at room temperature. In addition, perrhenate ions and methanol were formed as decomposition products of MTO in peroxide-containing solutions.[13] Because epoxides are also formed from the reaction of the monoperoxorhenium complex **A** with alkenes, reaction 3 is reversible.



A (3)

The reaction of the diperoxo−Re(VII) complex, **B** ([H_2O_2] = 0.5 M and [MTO] = 0.02 M), with styrene was complete in 3−4 h. Under the same conditions, in the absence of H_2O_2, the ^{1}H-NMR spectrum showed that less than 50% of the styrene oxide had reacted with MTO after 5 days. Because **A** and **B** exhibit similar reactivities toward the epoxidation of olefins,[9] these results indicate that the reverse rate constant in eq 3 is much larger than the forward one and so the equilibrium constant is much less than unity. In the presence of H_2O_2, **A** and **B** are present, so any alkene formed reacts rapidly with **A** or **B** and could not be observed. Oxygen was transferred from styrene epoxide (0.1 M) to 2,3-dimethyl-2-butene (0.1 M) in acetonitrile in the presence of MTO (0.02 M). The reaction produced styrene and 2,3-dimethyl-2-butene epoxide in ∼5−10% yield, eq 4. After 3 days, only ∼20% of styrene epoxide and 2,3-dimethyl-2-butene were consumed. Other products, 1-phenyl-1,2-ethanediol, 2,3-dimethyl-2,3-butanediol, and the bis(alkoxy)rhenium(VII) complexes, were also observed. In the absence of MTO, no styrene or 2,3-dimethyl-2-butene epoxide were observed, clearly substantiating the need for a catalyst.

(4)

2,3-Dimethyl-2-butene epoxide most probably results from the reaction of 2,3-dimethyl-2-butene with **A**, formed from

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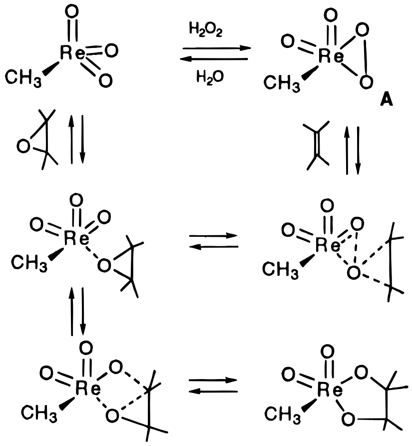
Scheme 1



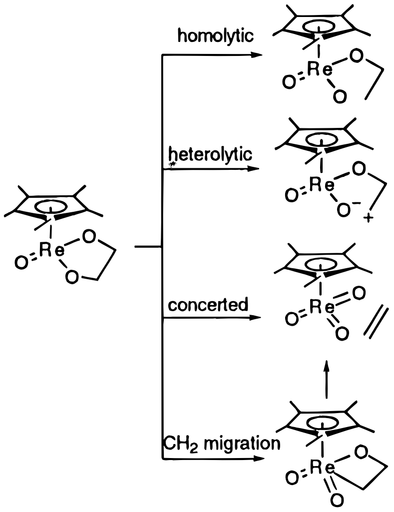
styrene epoxide with MTO as shown in eq 4. We have not explored the unimolecular reactions that lead to alkene release. On the other hand, the literature reports the slow unimolecular release of alkene from rhenium(V) diolates.[12,14]

The most substantial difference between Re(V) and Re(VII) diolates is not so much the oxidation state of the metal but the nature of the rhenium compound that remains were each diolate to dissociate an epoxide. The Re(V) compound would produce $R-ReO_2$, and Re(VII), MTO or $R-ReO_3$. The latter is a stable substance, whereas the former, although known,[5,15,16] is not particularly stable. On the other hand, were each diolate to dissociate an alkene, then the Re(V) compound would produce $R-ReO_3$, and Re(VII), the monoperoxide **A**, at least from a stoichiometric argument. Such differences must surely influence the transition state energies, favoring the Re(VII) compound in practice.

There is, we believe, a close interrelation of three processes: (a) alkene epoxidation with hydrogen peroxide catalyzed by MTO that proceeds through the peroxorhenium compound CH_3-$Re(O)_2(O_2)$, **A**; (b) diolate formation from an epoxide with MTO as described herein; and (c) alkene release from the diolate, which has been better characterized for Re(V).[12,14,17,18] In other words, eq 1 as well as eq 3 is reversible, since **A** is a an intermediate common to both.

The interrelationship between these processes, in part conjectural, is diagramed in Scheme 1. This diagram depicts the epoxidation occurring via the peroxide **A**, proceeding through one or more intermediates to either the epoxide or the diolate. In practice, epoxidation is very rapid, as is the conversion of MTO to **A** by reaction with hydrogen peroxide. Although not depicted, the diperoxo rhenium complex **B** would be expected to react in a parallel fashion. Thus diolate formation is of minimal importance until the supply of peroxide is exhausted (assuming the alkene was taken in excess); alternatively, as in the procedure described here, no peroxide was used, allowing the transformation of the epoxide to the diolate. Hydrogen peroxide accelerates the MTO-catalyzed ring opening reaction of epoxycyclohexane in *tert*-butyl alcohol−water solutions;[19] with MTO alone, ring opening is catalyzed but the reaction is slower.

Scheme 2



Certain possibilities for the excision of an alkene from a rhenium(V) diolate are shown in Scheme 2.[14,17,18] In particular, Hammett correlations have been used to rule out some possibilities, and CH_2 migration is the avenue suggested. By the same token, CH_2 migration (to O, not Re; see **IV**, a species with an extra O atom derived from **A**) may provide the avenue for the reaction under discussion here.

Experimental Section

A solution of methylrhenium trioxide (250 mg, 1 mmol) in 15 mL of dry methylene chloride was treated with the desired epoxide (1.2 mmol). After 1 day at room temperature, during which the solution changed from colorless to yellow to deep red, the solvent was removed under vacuum. The light yellow bis(alkoxy)rhenium(VII) compounds were purified by vacuum sublimation. These procedures were carried out under argon. 2,3-Dimethyl-2-butene epoxide was prepared as described,[20] and the other epoxides, available commercially, were purified using standard methods.[21]

Spectroscopic data for the isolated products in $CDCl_3$ are as follows.

(a) For $R_1 = R_2 = R_3 = R_4 =$ Me: ^{1}H-NMR δ 2.38 (3H), 1.34 (12H); ^{13}C-NMR δ 96.45 ($C-Me_2$), 42.70 (Me−Re), 25.75 (C−Me2); ^{1}H-NMR in CD_3CN δ 2.39 (3H), 1.36 (12 H).

(b) For $R_1 = R_2 = R_3 =$ H, $R_4 =$ Ph: ^{1}H-NMR δ 2.44 (3H), 4.15 (1H), 4.52 (1H), 5.35 (1H), 7.05 (5H); ^{13}C-NMR δ 136.54, 129.52, 128.85, 126.31, 87.18, 85.25, 42.83; ^{1}H-NMR in CD_3CN δ 2.45 (s, 3H), 4.78 (dd, 1H), 5.23 (t, 1H), 5.54 (dd, 1H), 7.32 (m, 3H), 7.47 (m, 2H).

(c) For the reaction between MTO and cyclododecane epoxide: ^{1}H-NMR δ 2.41 (3H), 4.24 (2H), 2.17 (4H), 1.82 (4H), 1.35 (8H), 1.01 (4H); ^{13}C-NMR δ 94.54, 42.07, 31.22, 28.73, 28.73, 26.18, 24.75, 22.83.

(d) For the reaction between MTO and *cis*-stilbene: ^{1}H-NMR δ 2.47 (3H), 4.31 (2H), 7.43 (10H); ^{13}C-NMR δ 134.69, 127.52, 126.03, 125.88, 98.76, 42.72.

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