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Bipyridine *N,N'*-Dioxide: A Felicitous Ligand for Methyltrioxorhenium-Catalyzed Epoxidation of Olefins with Hydrogen Peroxide

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Abstract: *Methyltrioxorhenium-catalyzed oxidation of olefins with hydrogen peroxide in the presence of bipyridine N,N'-dioxide gave epoxides in high yields, with no sign of formation of hydrolyzed diols.*

The epoxidation reaction is an important transformation of olefins, because epoxides are versatile electrophilic intermediates in organic synthesis. The use of transition metal complexes as the epoxidation catalyst is of particular interest,[1] due to their ability to activate oxidants such as molecular oxygen[2] and H_2O_2[3] which are environmentally benign. Methyltrioxorhenium (MTO) is rapidly emerging as a versatile catalyst, which is capable of oxidation of various functional groups in combination with H_2O_2 in high turnover numbers.[4] In spite of its high potentiality as an epoxidation catalyst,[5] MTO has not been employed as a synthetic tool because of the acidity of the MTO-H_2O_2 complex,[5b] which hydrolyzes the produced epoxide to give a diol.[6] In this context, Herrmann and his coworkers have reported that addition of tertiary amines suppresses the epoxide ring-opening process albeit the catalyst activity is also diminished.[5] Quite recently, Sharpless and his coworkers have reported that addition of 10-12 mol % of pyridine derivatives to 0.5 mol % of MTO suppresses the ring-opening without retarding the reaction rate.[7] Herein we wish to report a mild and efficient method for MTO-catalyzed epoxidation, in which bipyridine *N,N'*-dioxide has proven to be the ligand of choice for suppressing the acidity of the MTO-H_2O_2 complex without detrimental effect on catalyst activity.

At the outset, we employed a bipyridine derivative as a ligand to suppress the ring-opening in MTO-catalyzed epoxidation of stilbene. In accord with the observations of Herrmann, addition of bipyridine (1.2 mol %) to MTO (1.0 mol %) did suppress the ring-opening to afford epoxide in 70% yield whereas the yield was less than 20% without the additive. However, we were surprised to find that bipyridine was oxidized to give bipyridine *N,N'*-dioxide in quantitative yield at 20% conversion of stilbene.[8] Thus, we were intrigued by the feasibility of bipyridine *N,N'*-dioxide as a ligand for this epoxidation. Indeed, we were delighted to find that MTO (1.0 mol %)-mediated epoxidation of stilbene with 30% aqueous H_2O_2 (1.5 eq) in the presence of bipyridine *N,N'*-dioxide (1.2 mol %) in CH_2Cl_2 at rt proceeded smoothly to give 90% yield of stilbene oxide, with no sign of formation of hydrobenzoin. The result suggests that the real active species responsible for suppression of the acidity of the MTO-H_2O_2 complex is probably not bipyridine itself but bipyridine *N,N'*-dioxide, though its role is presently not clear.[9] Fortunately, suppression of catalyst activity was not observed in the presence of bipyridine *N,N'*-dioxide. In stark contrast, other *N*-oxides such as isoquinoline *N*-oxide or

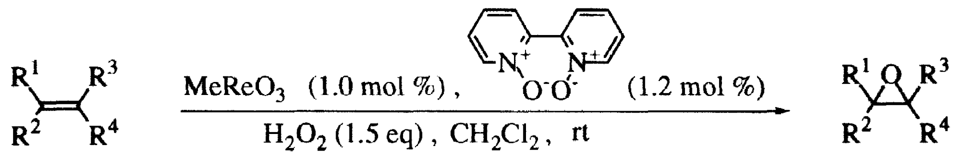

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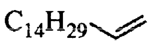
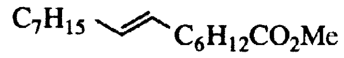
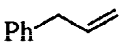
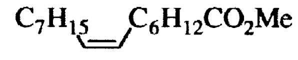
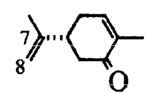
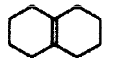
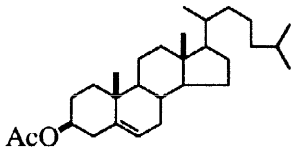
Table 1. MTO-Catalyzed Epoxidation with H_2O_2 in the Presence of 2,2'-Bipyridine *N,N'*-Dioxide.[a]

Olefin	Conditions	Yield,[b] %	Olefin	Conditions	Yield,[b] %
 (*E*:*Z*=>99 : <1)	rt, 24 h 40 °C, 5 h	90[c] 88[c]		rt, 12 h	95[f]
 (*E*:*Z*=3 : 97)	rt, 24 h	95[d]		rt, 24 h	91
 (*E*:*Z*=>99 : <1)	rt, 24 h 40 °C, 3 h	95[c] 92[c]		rt, 24 h	85
 (*E*: *Z*=1 : 99)	rt, 24 h	85[e]		rt, 24 h	96[g]
	rt, 2 h	80		rt, 12 h	94[h]

[a]Reaction condition: $c_{substrate}$ = 1 mol/L, 1.0 mol % MTO, 1.2 mol % bipyridine *N,N'*-dioxide, 1.5 eq 30% aqueous H_2O_2, CH_2Cl_2. [b]Isolated yield. [c]*cis*-Epoxide : *trans*-epoxide=<1 : >99. [d]*cis*-Epoxide : *trans*-epoxide=97:3. [e]*cis*-Epoxide : *trans*-epoxide=99:1. [f]3M H_2O_2 in *t*BuOH was employed. Aqueous H_2O_2 gave styrene oxide (70%) along with corresponding diol (20%). [g]7,8-Epoxide was formed as a 1:1 mixture of diastereomers. [h]α-Epoxide : β-epoxide=4 : 1

pyridine *N*-oxide were less effective (31% and 21% yields, respectively), which demonstrates that two oxygen atoms of bidentate dioxide are crucial for the success.

Epoxidations of various patterns of olefins with the present method are summarized in Table 1. As is evident from the data, the epoxidation employing bipyridine *N,N'*-dioxide as a ligand gives good to high yields of epoxides from mono-, di-, tri- and tetrasubstituted olefins. Particularly noteworthy is that monosubstituted olefins, except for styrene, are uneventfully oxidized to give epoxides in high yields, since it is documented that MTO-catalyzed epoxidation of these olefins remains a major challenge.[7b] Furthermore, epoxidation of styrene was found to give styrene oxide in 95% yield by employing 3 M H_2O_2 in *tert*-butyl alcohol instead of aqueous H_2O_2 as an oxidant; the homogeneous conditions gave virtually identical results with other olefins.

In summary, we have developed a highly efficient method for MTO-catalyzed epoxidation of olefins with H_2O_2 by exploiting bipyridine *N,N'*-dioxide as a ligand. Further studies on a catalytic, enantioselective epoxidation are currently in progress.[10]

References and Notes

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