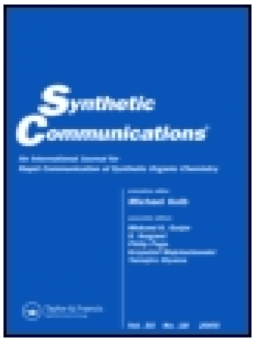

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COBALT(II) COMPLEX CATALYSED EPOXIDATION WITH MOLECULAR OXYGEN

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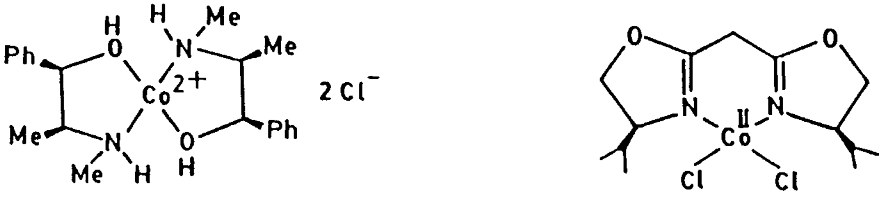
Abstract: *Cobalt(II) complexes* 1 *or* 2, *catalyses the epoxidation of alkenes in the presence of molecular oxygen and 2-methylpropanal in high yields.*

Transition metal complexes catalysed[1] epoxidation of olefins with molecular oxygen has received considerable attention from organic chemist in the last several years. These oxidations also enjoy paramount importance as mimics for various mono-oxygenases catalysed reactions in the biological systems. Recent work from Mukaiyama's and Katsuki's group have shown that these epoxidations can be made synthetically useful in the presence of a reductant like aldehyde.

In our previous communication[2], we have shown that cobalt(II) complexes mediate the oxygen atom transfer from molecular oxygen during coupling of carbonyl compounds with various olefins leading to the formation of various oxygenated products. In this communication, we describe the epoxidation of various olefins with molecular oxygen and 2-methylpropanal (Mukaiyama's condition) in the presence of catalytic amount of cobalt(II) complex[3] 1 and 2.



1 2

(Scheme 1)

The results of these epoxidations are compiled in table 1. Trans-stilbene can be smoothly converted to the corresponding epoxide in high yield. This epoxidation is quite facile for di- and tri substituted olefins as seen from the reaction of various dienes in presence of catalyst 1 or 2 (table 1, entry 3 & 5). Interestingly, the triene underwent smooth monoepoxidation at the trisubstituted unfunctionalised double bond (table 1, entry 8) in presence of catalyst 1 or 2. The epoxidation of the dienes and triene did not give any other mono or diepoxides under these conditions. Based on the epoxidation of these olefins, it can be seen that the order of reactivity of various double bonds under these conditions is: trisubstituted > allylic » terminal (monosubstituted). The conjugated diene like methyl sorbate gave a moderate yield of the monoepoxide (table 1, entry 10) in the presence of catalyst 2. Similarly the oxygenation of the acetates of cholesterol and diosgenin gave the corresponding epoxides as a mixture of diastereomers in high yields (table 1, entry 11 & 13).

In conclusion, the present route for epoxidation has an advantage over the method of Mukaiyama and Katsuki as (a) it can be performed at ambient temperature and at normal pressure of oxygen and (b) the dienes can be converted to monoepoxide exclusively. The study on the asymmetric epoxidation using chiral complex of **1** and **2** is currently underway in our laboratory.

Experimental Section

General Procedure : To a solution of olefin 3 (10 mmol) in 1,2-dichloroethane were added catalyst **1** (5 mol %) and 2-methyl propanal (20 mmol) and the resulting mixture is stirred under an oxygen baloon for 12-15 hrs. at ambient temperature. The reaction mixture is diluted with dichloromethane (50 ml), washed with saturated solution of sodium *bicarbonate*

Table I. Epoxidation of olefins using catalyst 1 and 2

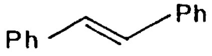
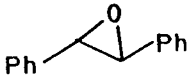
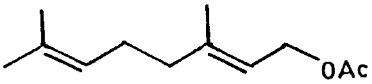
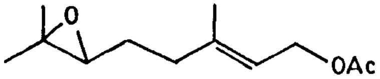
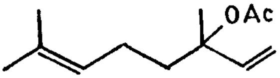
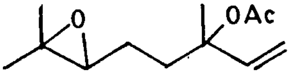
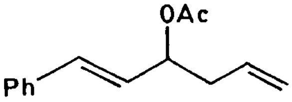
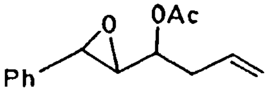
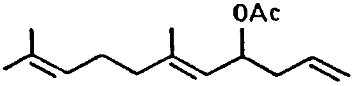
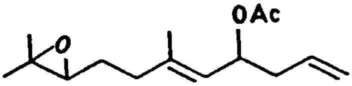
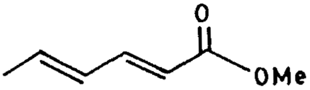
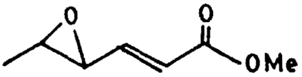
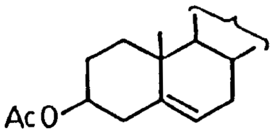
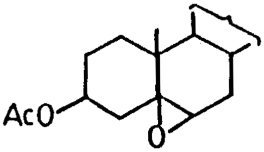
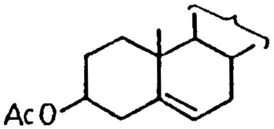
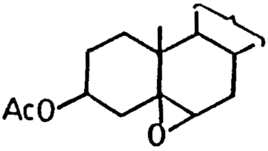
Entry	Olefin	Catalyst	Product (Yield %)^{a}
1	 **3a**	1	 **4a** (90)
2	**3a**	2	**4a** (86)
3	 **3b**	1	 **4b** (60)
4	**3b**	2	**4b** (63)
5	 **3c**	1	 **4c** (84)
6	**3c**	2	**4c** (92)
7	 **3d**	2	 **4d** (55)
8	 **3e**	1	 **4e** (25)
9	**3e**	2	**4e** (23)

Table I. Continued

10	 3f	2	 4f (13)
11	 Cholesteryl acetate 3g	1	 4g(89) α:β (76:24)
12	3g	2	4g(87)
13	 diosgenin acetate 3h	1	 4h(48)[b]
14	3h	2	4h(58)

a) isolated yields

b) a mixture of diastereomers obtained in a ratio of 81:19

and water. Drying ($MgSO_4$) and removal of solvent gave a residue which on column chromatography (SiO_2) yielded the epoxide **4**. These reactions were also performed with catalyst **2** as described above, however, dry acetonitrile instead of 1,2-dichloroethane was used as a solvent in this case. The solvent was removed under vacuo and diluted with ethyl acetate (50 ml) and the work-up procedure is same as described for the catalyst 1.

1-Acetoxy 3,7-dimethyl 6,7-epoxy oct-2-ene 4b. ^{1}H-NMR ($CDCl_3$) δ 5.35 (t, 1H), 4.55 (d, 2H), 2.8 (t, 1H), 2.35-2.0 (m, 2H), 1.9 (s, 3H), 1.8-1.5 (d, 5H), 1.2 (d, 6H). IR (Thin film) : ν_{max} 3040, 1730, 1660, 1370, 1230 cm^{-1}. Anal. calcd. for $C_{12}H_{20}O_2$: C, 73.42; H, 10.30. Found: C, 73.87; H, 10.51

3-Acetoxy 3,7-dimethyl 6,7-epoxy oct-1-ene 4c. ^{1}H-NMR ($CDCl_3$) δ 6.25-5.75 (dq, 1H), 5.3-5.0 (m, 2H), 2.7 (t, 1H), 2.0 (s, 3H), 1.6 (d, 4H), 1.2 (d, 6H). IR (Thin film) : ν_{max} 3100 , 1730, 1640, 1370, 1240 cm^{-1}. Anal. calcd. for $C_{12}H_{20}O_2$: C, 73.57; H, 10.31. Found: C, 73.56; H, 10.52

4-Acetoxy 5,6-epoxy 6-Phenyl hex-1-ene 4d. ^{1}H-NMR ($CDCl_3$) δ 7.1 (s, 5H), 4.5-6.0 (m, 4H), 3.55 (d, 1H), 2.9 (dd, 1H), 2.4 (t, 2H), 2.0 (s, 3H). IR (Thin film) : ν_{max} 3070, 1725 , 1630, 1360, 1230 cm^{-1}. Anal. calcd. for $C_{14}H_{16}O_3$: C, 72.41; H, 6.90. Found: C, 71.95; H, 6.82

4-Acetoxy 6,10-dimethyl 9,10-epoxy undec-1,5-diene, 4e. ^{1}H-NMR ($CDCl_3$) δ 6.0-5.5 (m, 8H), 5.3 (m, 5H), 2.75 (t, 1H), 2.3 (q, 2H), 2.1 (t, 2H), 2.05 (s, 3H), 1.8 (m, 5H), 1.35 (d, 6H). IR (Thin film) : ν_{max} 3080, 1730, 1635, 1370, 1240 cm^{-1}. Anal. calcd. for $C_{15}H_{24}O_3$: C, 71.43; H, 9.52. Found: C, 71.86; H, 9.48

Methyl 4,5-epoxy hex-2-enoate, 4f. ^{1}H-NMR ($CDCl_3$) δ 5.7-7.0 (m, 2H), 4.6 (s, 2H), 3.6 (s, 3H), 1.1 (d, 3H). IR (Thin film) : ν_{max} 3090, 1720, 1650, 1260 cm^{-1}. Anal. calcd. for $C_7H_{10}O_3$: C, 59.15; H, 7.04. Found: C, 60.02; H, 6.89

References and Notes

1. a) Groves, J.T.; Nemo, T.E., J. Am. Chem. Soc., 1983, 105, 5786. b) Groves, J.T.; J. Chem. Ed., 1985, 62, 928. c) Koola, J.D.; Kochi, J.K. Inorg. Chem. 1987, 26, 908. d) Wagler, T.R.; Fang, Y.; Burrows, C.J., J. Org. Chem., 1989, 54, 1584. e) Srinivasan, K.; Michaud, P.; Kochi, J.K., J. Am. Chem. Soc., 1986, 108, 2309. f) Kaku, Y.; Otsuka, M.; Ohno, M., Chem. Lett. 1989, 611. g) Marchon, J.-C.; Ramasseul R., Synthesis, 1989, 389. h) Matsuda, Y.; Koshima, H.; Nakamura, K., Murakami, Y.; Chem. Lett. 1988, 625. i) Yamada, T.; Takai, T.; Rhode, O.; Mukaiyama, T., Chem. Lett., 1991, 1. j) Irie., R., Ito, Y.; Katsuki, T., Tet. Lett., 1991, 32, 6891.

2. a) Iqbal, J.; Bhatia, B., Nayyar, N.K., Tetrahedron, 1991, 47, 6457. b) Bhatia, B.; Iqbal, J. Tet. Lett., 1992, 33, 7961.

3. a) Complex 1 is prepared by mixing ephedrine (A) (10 mmol) and dry $CoCl_2$ (5 mmol) in dry acetonitrile under nitrogen at ambient temperature. Satisfactory spectroscopic and elemental analyses were obtained for this complex. b) Complex 2 is prepared by mixing ligand (B) (prepared accordingly to ref. 3c) and $CoCl_2$ in

acetonitrile at room temperature and it was crystallised from acetonitrile to give satisfactory elemental analysis. c) Richard, E.L.; Abiko, A. and Masamune, S. Tet. Lett., 1990, 31, 6005.

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