Pergamon

Tetrahedron Letters, Vol. 35, No. 27, pp. 4847-4850, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

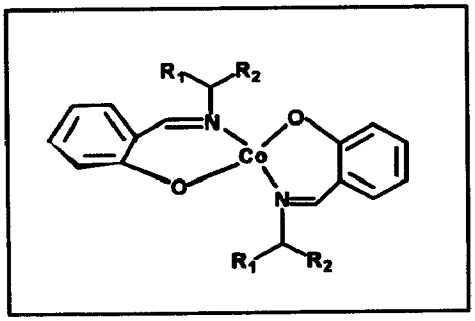
0040-4039(94)00892-2

Cobalt Catalyzed Oxidation of Secondary Alcohols with Dioxygen in the Presence of 2-Methylpropanal

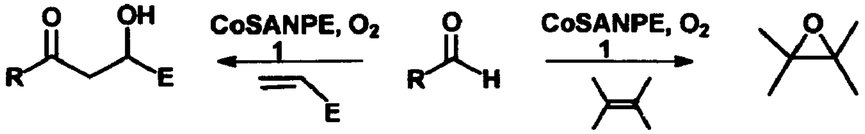
Swinder Jeet Singh Kalra, T. Punniyamurthy and Javed Iqbal*
Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, INDIA

Abstract: *Cobalt schiff base complex 2 catalyses the oxidation of a wide range of secondary alcohols to the corresponding ketones in the presence of dioxygen and 2-methylpropanal.*

Metal catalyzed oxidation of alcohols to carbonyl compounds in the presence of molecular oxygen constitutes[1] one of the most important and desirable chemical transformation. Considerations based on environmental pollution have imposed severe restrictions on the use of traditional oxidants for oxidation of alcohols to carbonyl compounds. These restrictions are imposed mainly to develop cleaner technologies with negligible inorganic salt formations and in view of these considerations, catalytic processes with optimal atom utilization seems to be an attractive proposition in achieving the above transformations. As a result to this, the oxidation of organic substrates by molecular oxygen in the presence of a metal catalyst provides the most formidable alternative to the existing mode of oxidations. Oxidation of alcohols to carbonyl compounds can be catalyzed with transition metals in the presence of various oxygen atom donors. We have earlier shown[2] that the cobalt-schiff base complex **1** (CoSANPE) acts as an excellent catalyst in oxidation and oxidative addition of alkenes in the presence of enolizable aldehydes (scheme I). We now show that the cobalt complex **2** (CoSANSE) acts as an

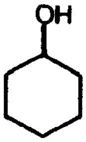
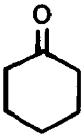
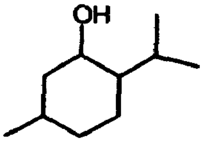
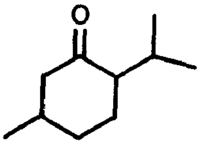
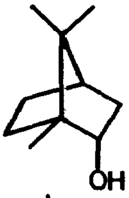
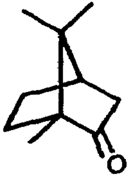
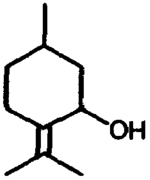
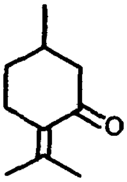
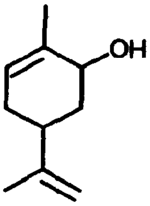
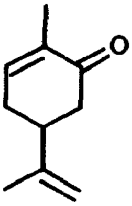
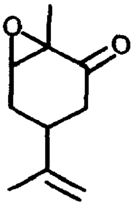
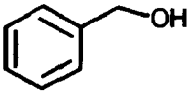
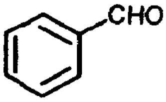
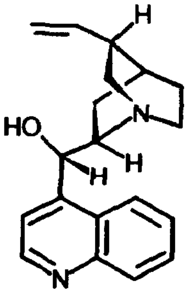
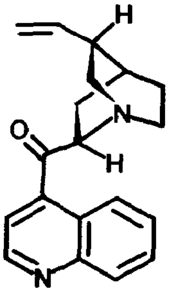


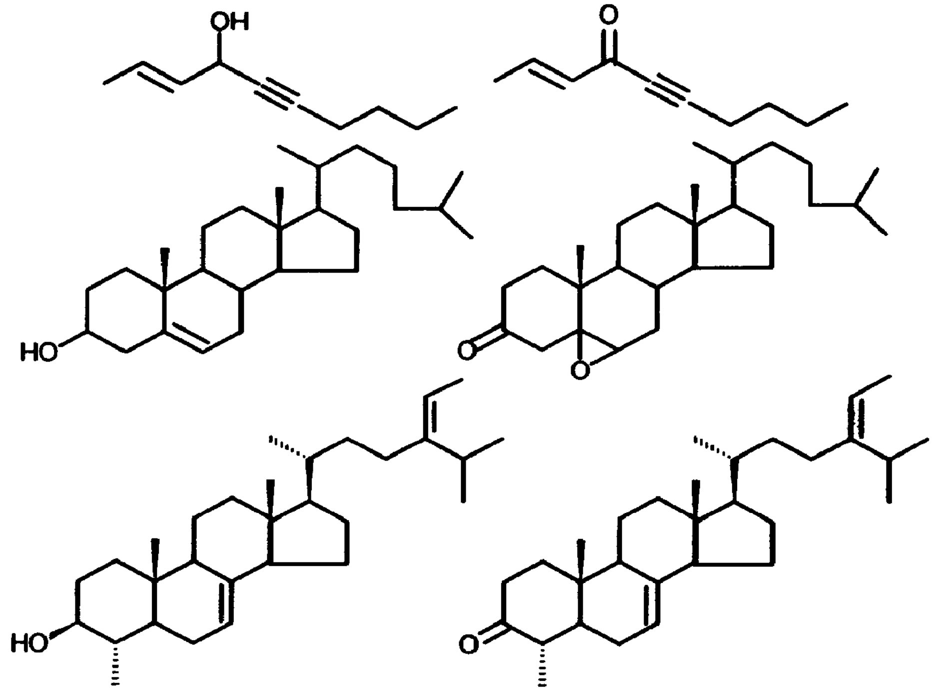
1. CoSANPE: R_1=Ph, R_2=Me.
2. CoSANSE: R_1=CH_2OH, R_2=CO_2Me



(SCHEME I)

Table I. CoSANSE Catalysed Oxidation of Alcohols with Molecular Oxygen

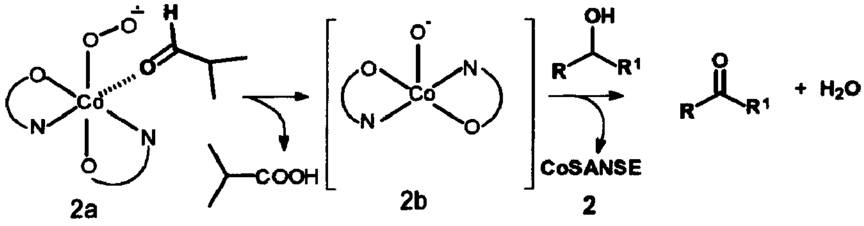
entry	alcohol	product	(yield %)^{a}
1			(79)
2			(76)
3			(70)
4			(72)
5		 	33:28 (61)
6			(78)^{b}
7			(38)



a*Isolated yields of carbonyl compounds.* b*Yield determined by HPLC.*

efficient catalyst in oxidizing various alcohols to the corresponding carbonyl compounds in the presence of dioxygen and isobutanal.

Typically, alcohol(5 mmol), isobutanal(10 mmol) cobalt complex **2** (5 mol%) were stirred in acetonitrile at ambient temperature in the presence of molecular sieves(3A) under dioxygen balloon for 15-17h. Removal of the solvent followed by aqueous workup and purification by distillation or chromatography afforded the corresponding carbonyl compounds along with isobutyric acid. Secondary cyclic alcohols ie. cyclohexanol and menthol underwent smooth oxidation to the corresponding ketones in good yields. Similarly, borneol was converted to camphor under these conditions (table I, entries 1-3). The cyclic allylic alcohol pulegol was oxidized to pulegone, however, carveol afforded mixture of carvone and the corresponding epoxy ketone as the major product (table I, entries 4 and 5). These reaction conditions are suitable for the oxidation of benzylic alcohols as evidenced by the conversion of benzyl alcohol to benzaldehyde and cinchonine to the corresponding ketones (table I, entries 6 and 7). Overoxidation of benzaldehyde may be avoided by careful monitoring of the progress of reaction and using a limited quantity (1 equivalent) of 2-methylpropanal. The acyclic alcohol is also prone to oxidation under these conditions to afford the corresponding enone in good yield (table I, entry 8). The oxidation of cholesterol in the presence of two equivalents of 2-methylpropanal affords the corresponding epoxy ketone as a mixture of diastereomers (table I, entry 9), surprisingly, the selective oxidation to cholestenone could not be achieved by using one equivalent of 2-methylpropanal. Interestingly, α_1-sitosterol underwent selective oxidation to give the corresponding ketone in good yields(table I, entry 10). These reactions are facilitated by the presence of molecular sieves (3A) which reduces the reaction time considerably. A plausible explanation for these oxidations may be given by assuming an initial formation of the cobalt peroxy complex in the presence of aldehyde. An EPR study has indicated that the superoxy complex 2a is formed only when aldehyde is present in the reaction mixture (scheme II) and the g-value (2.0167) obtained clearly supports the formation of the monomeric superoxy species. It is conceivable that the coordination of the aldehyde to the metal will enhance the oxidizability of the latter which may give rise to the formation of the peroxy complex. A similar observation by Basolo and coworkers[3] in related cobalt complex with different pyridine bases provides strong supports to our proposal. It is also shown recently[4] that aldehydes facilitates the formation of metal peroxy complexes derived from nickel and cobalt. An intramolecular oxygen transfer to aldehyde via complex 2a would provide the carboxylic acid and the cobalt oxo species 2b which may subsequently oxidize the alcohol to the corresponding carbonyl compound and water and in the process, the catalyst 2 will be regenerated to complete the cycle.



(SCHEME II)

We have demonstrated that the cobalt complex 2 is an efficient catalyst for the oxidation of alcohols with dioxygen in the presence of 2-methylpropanal. Work is in progress to delineate the mechanism of these reactions.

References

1. (a) Sheldon,R.A.; Kochi,J.K. *Metal Catalyzed Oxidations of Organic Compounds;* Academic Press: New York, **1981**, and references therin. (b) Mimoun,H. *Comprehensive Coordination Chemistry;* Pergamon Press: Oxford, Vol.6, **1987.** (c) Tovrog,B.S.; Diamond,S.E.;Mares,F.; Szalkieiez, A. *J. Am. Chem.Soc.*, **1982,** 104, 4268. (e) Kanemoto,S.; Saimoto,H.H.; Oshima,K.; Nozaki, H. Tetrahedron Lett., **1984,** 25, 3317. (f) Tanaka, M.; Kobayashi,T.; Sakakura,T. *Angew Chem.* **1984,** 96, 519. (g) Murahashi,S.-I.; Naota, T.; Hirai, N. *J. Org. Chem.* **1993,** 58, 7318.

2. (a) Bhatia,S.; Punniyamurthy,T.;Bhatia,B.; Iqbal,J. *Tetrahedron,* **1993,** 49, 6101. (b) Punniyamurthy, T.; Bhatia,B.; Iqbal,J. *J. Org. Chem.* **1994,** 59, 850. (c) Punniyamurthy, T.; Iqbal,J. *Tetrahedron Lett.* **1994** (in press).

3. For the formation of oxygen adduct from cobalt schiff base complexes see: (a) Crumbliss,A.L.; Basolo,F. *J. Am. Chem. Soc.* **1970,** 92, 55. (b) Mimoun,M. *Comprehensive Coordination Chemistry;* Pergamon Press: Oxford, **1987,** Vol.6, p317.

4. Nishida.;Fujimoto,T.;Tanaka,N.*Chem. Lett.* **1992,** 1291.

(*Received in UK* 7 *April* 1994; *accepted* 6 *May* 1994)