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Cobalt(II) Schiff's Base Complex Catalysed Oxidation of Alcohols with Dioxygen in the Presence of Ethyl 2-oxocyclopentanecarboxylate

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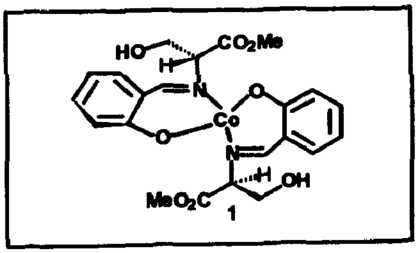
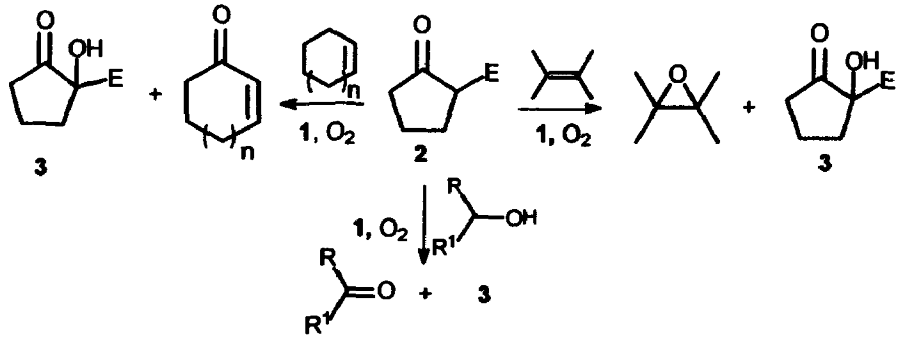
Abstract: *Cobalt(II) Schiff's base complex* 1 *catalyses the oxidation of primary and secondary alcohols to aldehydes and ketones respectively, in the presence of dioxygen and ethyl 2-oxocyclopentanecarboxylate* 2 *at 60-70° C.*

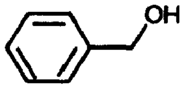
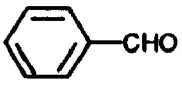
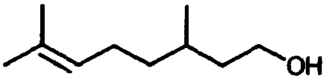
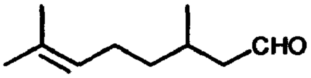
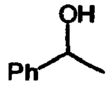
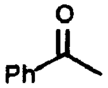
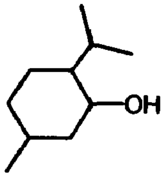
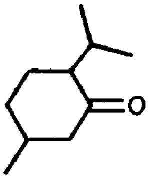
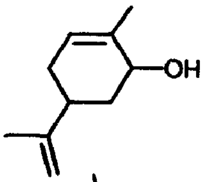
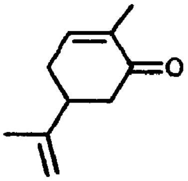
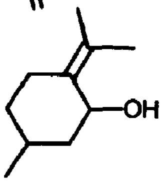
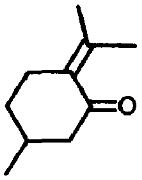
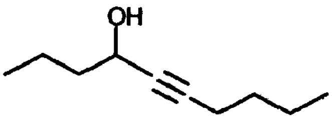
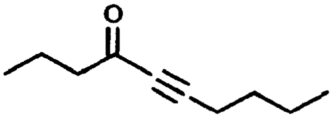
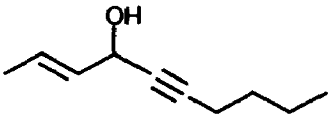
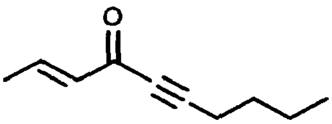
Transition metal catalysed oxidation of organic substrate with dioxygen is an area of current interest[1] to synthetic and mechanistic chemists. Impressive advances have been made to provide deeper insight into the intricacies involved during oxygen activation and its subsequent reaction with organic molecules. We have recently demonstrated[2a] that cobalt(II) Schiff's base complex 1 catalyses the oxygenation of alkenes in the presence of ethyl 2-oxocyclopentanecarboxylate 2 and dioxygen to epoxides or in certain cases to the corresponding allylic alcohols or enones. We now show that a variety of primary and secondary alcohols can be oxidised[3] to the corresponding aldehydes and ketones respectively, in the presence of 2, dioxygen and cobalt(II) catalyst 1 (Scheme I). A preliminary account of these findings is described below





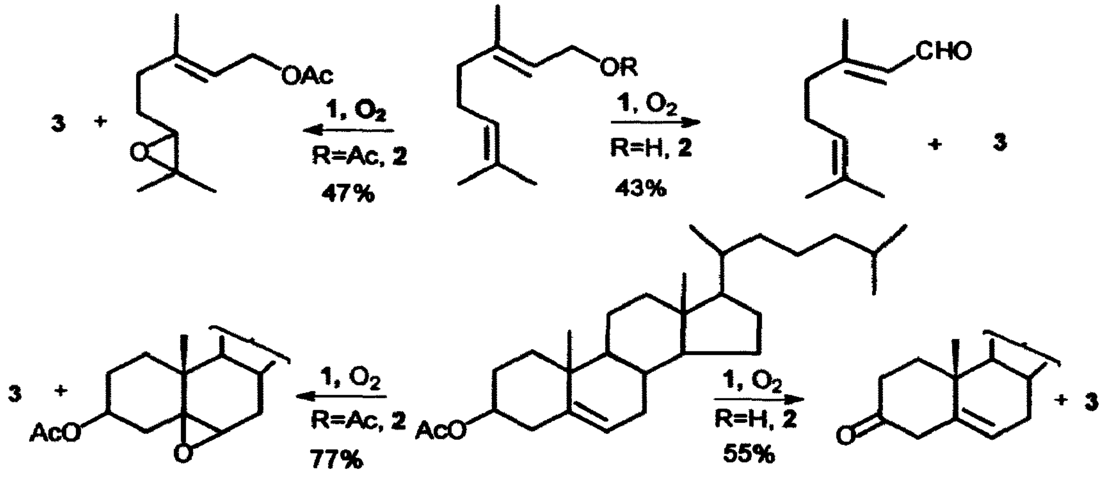
(SCHEME I)

TableI. CoSANSE Catalysed Oxidation of Alcohols with Molecular Oxygen

entry	alcohol	product	(yield %)[a]
1			(82)[b]
2			(49)[b]
3			(85)[b]
4			(72)
5			(61)
6			(59)
7			(44)
8			(51)

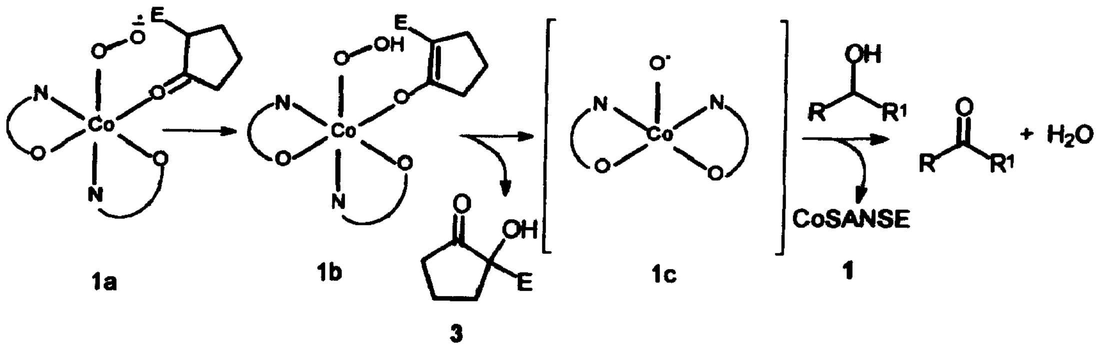
[a] Isolated yields of the carbonyl compounds. [b] Yield determined by HPLC

Alcohols(2.5 mmol), **2** (5 mmol) and cobalt(II)[2b] complex **1** (5 mol %) were heated at 60-70° C in acetonitrile under dioxygen balloon for 15-17 h . Removal of the solvent followed by aqueous work-up and chromatography afforded the corresponding aldehyde or ketone along with tertiary alcohol in high yields (table I). Thus, benzyl alcohol and citranellol were oxidised in high yields to the corresponding aldehydes which did not undergo further oxidation to carboxylic acids (table I, entries 1-2). 1-Phenylethanol, menthol, carveol and pugelol underwent smooth oxidation to the corresponding ketones in high yields (table I, entries 3-6). Similarly, propargylic and enyne alcohols are smoothly oxidised to the correseponding ketones in good yields (table I, entries 7 and 8). These transformations can also be carried out at ambient temperature, however, longer reaction time is required for the completion of the reactions. It is also noteworthy that the primary alcohols are oxidised slowly as compared with the secondary ones. Presence of molecular sieves facilitates the reaction as high conversion of alcohol to ketone is observed under these conditions. Interestingly, the olefinic alcohols can be selectively transformed to either the corresponding carbonyl compounds or epoxides under these experimental conditions. Thus geraniol can be converted to citral by using equivalent amount of **2** and catalyst**1** whereas geranyl acetate can be transformed to the corresponding epoxide in high yield (scheme 2). A similar treatment on cholesterol provides the formation of cholestenone whereas cholesteryl acetate undergoes transformation to a mixture of epoxides in good yields (scheme II). The flexibility permitted by this transformation will be of great importance in achieving selective conversion of olefinic alcohols. These oxidations may be proceeding via a cobalt superoxide complex whose formation is facilitated by **2** which acts as a reductant . An EPR study of this reaction has indicated that the superoxide complex **1a** is formed only when **2** is present in the reaction mixture (scheme III). The g-value obtained from the EPR of the reaction mixture clearly supports the formation of the monomeric cobalt-superoxide species[4]. It is clear that the coordination of **2** with the metal will enhance the oxidisiblity of the latter



(SCHEME II)

and this will result in the formation of the oxygen adduct 1a. These observations are in accord with the results obtained by Basolo and coworkers in related cobalt-complex with different pyridine bases. We believe that the cobalt-oxygen complex 1a may transform to the corresponding enolate complex 1b via an intramolecular hydrogen abstraction. Rapid intramolecular hydroxylation of the cobalt enolate complex 1b will provide 3 and cobalt-oxo species 1c which may subseqeently oxidise the alcohols to the corresponding carbonyl compounds and in the process the catalyst 1 will be regenerated[2b] to complete the cycle.



(SCHEME III)

In conclusion, Cobalt(II) complex 1 catalysed oxidation of alcohols with dioxygen and 2 provides a very effective and mild route to aldehydes and ketones.

References and Notes

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