

Oxidation of primary amines with dioxygen catalysed by an oxygen carrier cobalt(II) Schiff base chelate, CoSMDPT[†]

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Abstract. Cobalt(II) bis[3-(salicylideneamino) propyl] methylamine, (CoSMDPT) catalysed the oxidation of primary amines with dioxygen. The oxidation of benzylamine, 4-methylbenzylamine and 4-methoxybenzylamine gave aldehyde intermediates which reacted with the starting amines to yield the corresponding Schiff bases as the final products. The oxidation of 1-phenylethylamine gave 2,4,6-triphenyl-3-aza-3,5-heptadiene by disproportionation of the intermediate Schiff base, 2,4-diphenyl-3-aza-3-heptene.

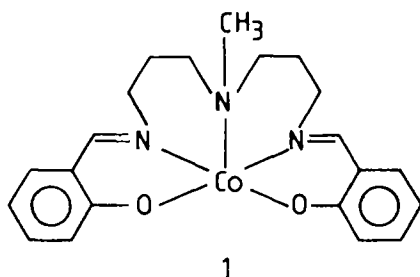
Keywords. Dioxygen; oxidation of primary amines; cobalt(II) bis[3-(salicylideneamino) propyl] methylamine.

1. Introduction

Activation of dioxygen by reversible coordination to transition metal chelates and its transfer to organic compounds is of considerable importance owing to its application in organic synthesis and in furthering our understanding of the chemistry of biological oxidations (Jones *et al* 1979; Sheldon and Kochi 1981). Of particular interest are cobalt(II) Schiff base chelates which can effectively catalyse the oxidation of phenols (Sheldon and Kochi 1981), indoles (Nishinaga 1975), hydrazones (Inada *et al* 1982), stilbenols (Ganeshpure and Satish 1988) and secondary amines (Nishinaga *et al* 1988). Metal catalysed oxidation of amines is of interest because of its relevance to the enzymatic degradation of nitrogen-containing compounds in biological systems (Murata *et al* 1989). A number of reagents/catalysts have been reported in the oxidation of amines to give a variety of products depending on the nature of the oxidizing agent (Tang *et al* 1978; Moriarty *et al* 1988; Nishinaga *et al* 1988; Porta *et al* 1989; Capdevielle *et al* 1990). However, oxidation of primary amines with dioxygen using oxygen carrier cobalt(II) chelates as catalysts does not appear to be investigated. In continuation of our work on activation of dioxygen and its transfer to organic substrates (Satish *et al* 1985; Satish and Ganeshpure 1986; Ganeshpure and Satish 1988, 1989), we now report the oxidation of primary amines with dioxygen promoted by a pentacoordinate cobalt(II) Schiff base chelate, cobalt(II) bis[3-(salicylideneamino) propyl] methylamine, CoSMDPT (1).

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2. Experimental

The IR spectra were recorded on a Beckmann IR 4220 spectrometer. The NMR spectra were recorded as CDCl_3 solutions on a Jeol FX 100 spectrometer. The NMR chemical shifts are in the δ scale. Elemental analyses were carried out on a Carlo-Erba C, H, N autoanalyser. Yield refers to pure isolated material.

2.1 Materials

4-Methylbenzylamine and 4-methoxybenzylamine were prepared by catalytic hydrogenation of 4-methylbenzaldehyde oxime and 4-methoxybenzaldehyde oxime, respectively, in the presence of Pd-C 5%. 1-Phenylethylamine was prepared from acetophenone as per Vogel (1978). N-Benzylaniline was prepared by catalytic hydrogenation of N-benzylideneaniline. All the substrates were freshly purified by vacuum distillation and stored under a nitrogen atmosphere.

CoSMDPT was prepared by the literature procedure (Drago *et al* 1980) and satisfactory elemental analysis of C, H, N was obtained. Acetonitrile AR grade was purified by the literature method and stored over molecular sieve 5A°. High purity oxygen gas from M/s. Indian Oxygen was used.

2.2 Procedure for catalytic oxidation reaction

In a typical experiment, an amine (10 mmol) was added to a solution of CoSMDPT (205 mg, 0.5 mmol) in acetonitrile (15 ml) and the resulting solution stirred magnetically at room temperature under an atmosphere of dioxygen. After 6 h, the reaction mixture was diluted with ether (30 ml) and the metal complex was separated by passing the mixture through a short column of silica gel. The catalyst-free reaction mixture was evaporated and the products were separated by column chromatography over silica gel. The yields of the reaction products are reported in table 1. The balance comprised unreacted starting materials. In the case of 1-phenylethylamine, a minor product beside (6) was not isolated. The products (3a-c, 6) were characterized by IR and NMR studies (table 1) and compared with authentic samples of 3a-c.

3. Results and discussion

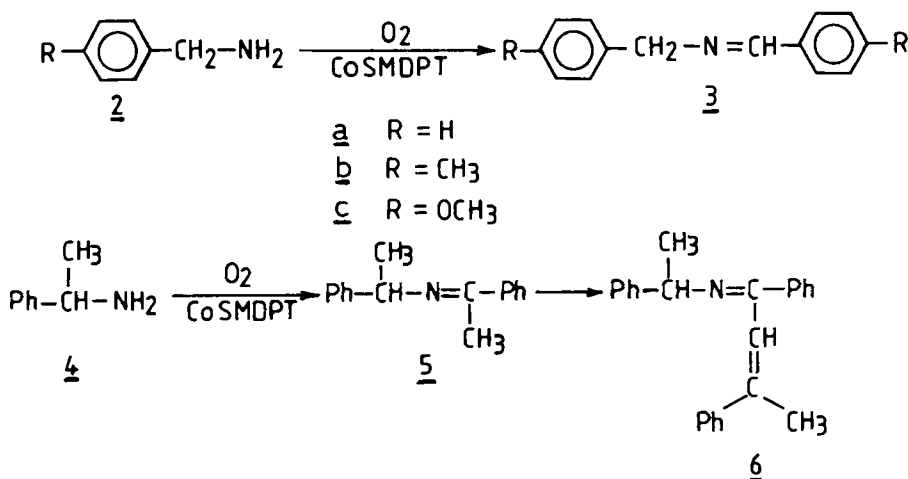
The results of the oxidation reaction are shown in table 1. Oxidation of benzylamine with dioxygen in the presence of CoSMDPT gave N-benzylidenebenzylamine (3a)

Table 1. Oxidation of amines with molecular oxygen catalysed by CoSMDPT.

Amine	Product*	Yield** (%)	IR (cm ⁻¹) (neat)	¹ H-NMR†
Benzylamine	<u>3a</u>	42	1630	4.8(s, 2H, CH ₂), 6.79–7.31 (m, 10H, aromatic) and 8.4(s, 1H, CH)
4-Methylbenzylamine	<u>3b</u>	34	1630	2.33(s, 3H, CH ₃), 2.42 (s, 3H, CH ₃), 4.73(s, 2H, CH ₂), 6.7–7.3(m, 8H, aromatic) and 8.33(s, 1H, CH)
4-Methoxybenzylamine	<u>3c</u>	32	1625	3.69(s, 3H, OCH ₃), 3.73 (s, 3H, OCH ₃), 4.64(s, 2H, CH ₂), 6.7–7.2(m, 8H, aromatic) and 8.22(s, 1H, CH)
1-Phenylethylamine	<u>6</u>	12	1630	1.63(d, j=6, 3H, CH ₃) 2.09(s, 3H, C=C-CH ₃), 4.54(q, j=6, 1H, N-CH), 6.75–7.38(m, 15H, aromatic) and 8.33(s, 1H, olefinic CH)
N-Benzylaniline	<u>8</u>	8	1625	

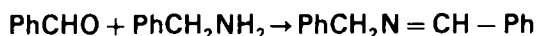
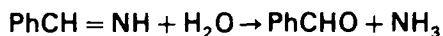
* All the products were oils; ** Based on amine taken; † s – singlet; d – doublet; q – quadruplet; m – multiplet.

(scheme 1). No reaction occurred when either dioxygen or CoSMDPT was excluded, indicating that both catalyst and oxidant are essential for the reaction. The formation of the product (3a) can be explained on the basis of initial oxidation of benzylamine to benzaldehyde which reacts with benzylamine to give the Schiff base (3a).

**Scheme 1.**

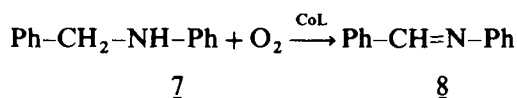
Porta *et al* (1989) have reported the formation of N-benzylidenebenzylamine by oxidation of benzylamine with iodobenzene. In the proposed mechanism (scheme 2), benzylamine on oxidation forms an imine intermediate which reacts with a water molecule to form benzaldehyde. In the next step benzaldehyde reacts with benzylamine

to give the Schiff base.



Scheme 2.

In the present system, the CoSMDPT-dioxygen adduct, LCoOO probably abstracts the α -hydrogen of benzylamine initiating the reaction. The resulting cation radical on deprotonation and further oxidation gives the imine. Nishinaga *et al* (1988) have proposed a similar mechanism for oxidation of secondary amines to Schiff bases (e.g. 7 \rightarrow 8) using dioxygen and cobalt(II) chelates.



We observed that N-benzylaniline (7) on oxidation with dioxygen in the presence of CoSMDPT under our experimental condition gave benzylideneaniline (8) in 8% yield.

Similarly, 4-methylbenzylamine (2b) and 4-methoxybenzylamine (2c) on oxidation gave the Schiff bases (3b) and (3c) respectively.

Oxidation of 1-phenylethylamine under these conditions gave the compound (6). 1-Phenylethylamine probably gives the Schiff base (5) by a route similar to benzylidenebenzylamines. The Schiff base (5) on disproportionation yields (6) and 1-phenylethylamine. Schaefer and Zimmermann (1970) have reported spontaneous disproportionation in the above manner for Schiff bases having methylene or methyl group adjacent to the carbon of N=C.

Under the conditions of our experiments, cyclohexylamine and 2,6-dimethylaniline were found to be unreactive whereas 2-phenyl-ethylamine gave a complex mixture of products (conversion 12%).

4. Conclusion

This work describes a hitherto unknown application of CoSMDPT, a versatile dioxygen activating chelate, as a catalyst for oxidation of benzylamines to give Schiff bases in a single-step reaction.

Acknowledgements

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