Molecular Oxygen Insertion into Picolyl, Thenyl, Furyl and Furfuryl Cobaloximes under Thermal and Photochemical Conditions and their Decomposition Studies

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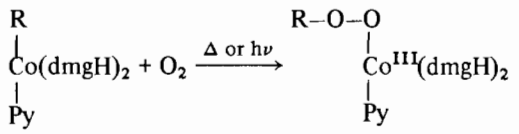
Abstract

Some new picolyl, thenyl, furyl and furfuryl cobaloximes have been synthesized. The insertion of molecular oxygen into the Co–C bond occurs readily under photochemical stimulation but there is no insertion under heating. The thermal decomposition of the inserted product in benzene and methanol forms aldehydes and alcohols.

Introduction

There are many reports of the insertion of molecular oxygen into the Co–C bond of an organocobaloxime to yield 1:1 dioxy adducts [1]:



(Py = pyridine; dmgH = dimethylglyoxime monoanion; R = allyl, benzyl, alkyl)

The insertion proceeds thermally in the dark, or in the case of benzylic or allylic derivatives, photochemically, but alkyl compounds do not react even at moderate temperatures unless irradiated [2]. Several ESR, kinetics and stereochemical studies of the mechanism of the reaction have been made [3] and recently the insertion has been shown to occur with racemisation at α carbon [4]. In this paper we report the synthesis of some new organocobaloximes in which the cobalt-bound carbon belongs to a heterocyclic group and a study of their thermal and photochemical reaction with molecular oxygen. The decomposition of the inserted products in benzene and methanol is also studied. The work is of interest because of the structural similarities to vitamin B_{12} chemistry.

Experimental

2- and 3-thenyl bromide were prepared by the literature methods [5, 6]. Furfuryl alcohol was brominated with PBr_3 in ether according to the method by Zanetti [7]. Since pure furfuryl bromide is very unstable, its ethereal solution was used in the cobaloxime preparation. 3-furyl bromide was prepared from propagyl alcohol as outlined by Tada *et al.* [8]. 2-picolyl bromide was prepared by four step synthesis from 2-picoline [9]. Tosylation of 2-picolyl alcohol was carried out as described by Klamann *et al.* [10]. $Co^{I}(dmgH)_2Py$ was made either by Schrauzer's disproportionation method or by reduction of chlorocobaloxime by $NaBH_4$ [11].

Reaction of Molecular Oxygen with Organocobaloximes

In a typical experiment a solution of the organocobaloxime (20 mmol in 20 ml CH_2Cl_2) at 0–5 °C was irradiated with two 250 W tungsten lamps at approximately 10 cm distance and oxygen was bubbled through the solution. The reaction was monitored by TLC using ethyl acetate as the solvent. The reactions were completed within one hour in all cases. The product was isolated on a preparative TLC plate using ethyl acetate as the eluent. The yields were quantitative in all cases.

Decomposition Studies

In a typical reaction, 10 mmol of the cobaloxime in 20 ml of benzene or methanol was refluxed under nitrogen atmosphere. The reaction was over within 6–8 h. The solvent was evaporated and the organic product was extracted with solvent ether and subjected to gas chromatography for analysis.

Physical Measurements and Instruments

^1H NMR spectra were recorded on 60 MHz (Jeol PMX-60) and 90 MHz (Varian EM-390). UV-Vis absorption spectra were recorded on Cary-17D at ambient temperature. The product ratios from decomposition studies were analysed by gas chromatography (CIC Model, ACI-F1). The elemental analyses were undertaken at the Regional Sophisticated Instruments Centre, Lucknow.

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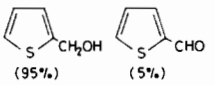
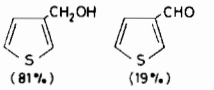
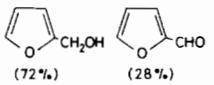
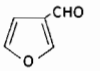
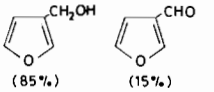
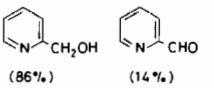
TABLE I. Spectra and Analysis of $RCo(dmgH)_2Py$ and $ROOCo(dmgH)_2Py$.

Compound	Yield (%)	^1H NMR ($CDCl_3$)δ			Py			Analysis: found(calc.) (%)			$\lambda^{nm}_{CH_3OH}$ (log ε)
		Aromatic	CH_2	dmgH	α	β	γ	C	H	N	
1a	52	6.65, 7.00	3.00	2.05	7.20	7.65	8.50	46.02 (46.45)	5.10 (5.18)	14.98 (15.05)	385, (3.42); 281, (3.12); 240, (3.49)
2a	[a]	6.80, 7.15	4.45	2.25, 2.35	7.15	7.60	8.30	43.35 (43.47)	4.80 (4.86)	13.98 (14.08)	237, (3.28); 247, (3.42); 322, (2.92)
1b	49	6.75, 7.20	2.85	2.00, 2.10	7.30	7.70	8.50	46.75 (46.45)	5.05 (5.18)	15.92 (15.05)	359, (3.20); 277, (3.21); 239, (3.60)
2b	[a]	7.15, 7.25	4.30	2.25, 2.35	7.10	7.60	8.30	43.43 (43.47)	4.80 (4.86)	13.92 (14.08)	231, (3.34); 244, (3.51); 312, (2.96)
1c	42	6.00, 7.40	2.40	2.00	7.30	7.75	8.60	48.00 (48.15)	5.35 (5.60)	15.48 (15.59)	383, (3.39); 284, (3.18); 239, (3.58)
2c	[a]	6.15, 7.15	4.25	2.30, 2.40	7.15	7.60	8.30	44.80 (44.92)	5.12 (5.02)	14.65 (14.56)	224, (3.11); 259, (2.86); 316, (2.52)
1d	50	6.00, 7.12	2.55	2.00, 2.10	7.15	7.75	8.42	48.20 (48.15)	5.30 (5.60)	15.40 (15.59)	348, (3.22); 286, (3.31); 238, (3.56)
2d	[a]	6.30, 7.20	4.15	2.25, 2.35	7.20	7.60	8.25	44.82 (44.92)	4.98 (5.02)	14.45 (14.56)	242, (2.98); 254, (3.20); 324, (2.61)
Ie	10[b]	7.00, 8.25	2.85	2.05	7.30	7.60	8.55	49.35 (49.57)	5.40 (5.48)	18.05 (18.25)	445, (2.75); 330, (3.42); 285, (3.52)
2e	[a]	7.10, 7.45, 8.20	4.40	2.25, 2.35	7.15	7.55	8.25	46.30 (46.35)	5.10 (5.12)	17.10 (17.07)	242, (3.31); 254, (3.31); 315, (2.81)

[a] Quantitative. [b] With tosylate = 60%.

TABLE II. Organic Products[a] from the Decomposition of $RCo(dmgH)_2Py$ (1a–1e) and $ROOCo(dmgH)_2Py$ (2a–2e).

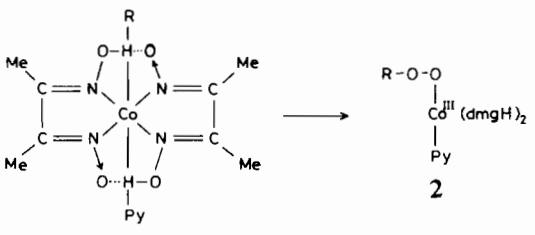
Compound	Benzene/ Methanol	Compound	Benzene	Methanol
1a		**2a**		 (95%) (5%)
1b		**2b**		 (81%) (19%)
1c		**2c**		 (72%) (28%)
1d		**2d**		 (85%) (15%)
1e		**2e**		 (86%) (14%)

[a] All products were analysed by gas chromatograph using 10% SE-30 Crom-P (85-100 M) 2 m long column.

Results and Discussion

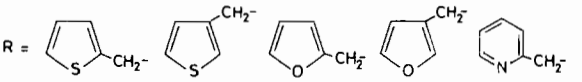
The reactions of picolyl, thenyl, furyl and furfuryl halides with bis(dimethylglyoximato)pyridinecobalt-(I) ion in methanol were very fast and smooth. However, when the hydrobromide salt of 2-picolyl bromide was used*, the yield of the product required was very poor due to the formation of a species produced by attack of $Co^{I}(dmgH)_2Py$ on the most electrophilic quaternary nitrogen atom**. However, the reaction of 2-picolyl tosylate gave reasonable yield (see Table I) but was visibly slower compared to the bromide. This observation is justified since the tosyl group is weak and the leaving group is hard, thus SN_2 reaction of tosylate with soft and bulky cobaloxime must be slow. SN_2 is the accepted mechanism for the formation of cobaloximes from primary halides and tosylates [11, 12].

The molecular oxygen insertion into Co–C bond of **1a–1e** under photochemical stimulation is observed to be one of the fastest insertion reactions studied so far in cobaloximes:



1 **2**

*,**See right hand column.

R = 

(a) (b) (c) (d) (e)

In contrast, no insertion product was formed even after 20 h heating at 40 °C. However, it was observed that, after 40 h, homolysis of Co–C bond followed by atom abstraction from the solvent led to the formation of three new cobaloximes. The atom abstraction process was much faster in chloroform at 45 °C (≈4 h) and formed two new cobaloximes. It was also observed that the ratio of the formation of products was dependent upon temperature, oxygen pressure etc. [13]. This observation, that homolysis followed by atom abstraction from solvent gives rise to new Co–C bond formation, is of particular interest when considered in relation to the reaction mechanism of the vitamin B_{12} dependent dehydrase [14].

The ^1H NMR spectra of the dioxy adducts **2a–2e** are very interesting, and show the nonequivalence of four methyl groups on dimethylglyoxime (equatorial ligands) in all cases, two methyl signals appearing in 3:1 ratio about 0.1 ppm apart (see Table I). Since allyl, alkyl, benzyl dioxycobaloximes do not react in the same way, this must be due to the presence of heteroatom in the axial organic ligand. This has been

*Picolyl bromide is very unstable and difficult to obtain in pure form; its recovery from the hydrobromide salt is very poor.

**^1H NMR ($CDCl_3$): 4.52 ($-CH_2$), 2.0 (4 CH_3); *Anal.* (calc.(found)): C, 42.30 (42.2); H, 4.8 (4.6); N, 15.4 (15.65); Br, 14.65 (14.75) %.

attributed to the formation of a hydrogen bond between the oxime hydrogen and the heteroatom of the axial organic ligand [15].

The organic products obtained from the decomposition of **1a**–**1e** and **2a**–**2e** point to the involvement of R and ROO$^{\bullet}$ radicals (Table II). Similar products have also been obtained in earlier studies [16]. However, further investigations are being carried out to determine the exact mechanism of the formation of aldehydes and alcohols from the decomposition of **2a**–**2e**.

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