Halogenolysis of *para*-Substituted Benzyl Cobaloximes. Part II.*

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Abstract

The reaction of benzyl cobaloximes with halogens (Cl_2 or Br_2) in chloroform or acetic acid forms benzyl halides and benzyl ethers of dimethylglyoximes by an oxidative dealkylation mechanism.

Introduction

The reaction of halogens with organo cobalt(III) complexes is of considerable interest in view of the many proposed mechanisms for the cleavage of Co–C bond [1]. Halogenation has been shown to occur by an oxidative dealkylation mechanism, consisting of an oxidation to organo cobalt(IV) species, followed by a carbocation transfer to a nucleophilic acceptor, a free radical and direct electrophilic mechanism [2, 3]. Of all the organocobalt(III) complexes, the halogenation of benzyl cobaloximes appears to be more complicated. In view of the chemical oxidation potential data on various substituted benzyl cobaloximes, which vary significantly with the nature of the axial organic ligand [4], it is anticipated that an extension of such studies to that series might help in differentiating between the above mechanisms. We are presenting unambiguous evidence of the oxidative dealkylation mechanism in this paper.

Experimental

Benzyl cobaloximes were prepared according to the procedure in the literature, from cobaloxime(I) and organic halides. The cobaloxime(I) was generated *in situ* by anaerobic alkaline disproportionation of cobaloxime(II) in methanol as described by Schrauzer [5].

Reaction of Halogens with Benzyl Cobaloximes

In a typical experiment, a bromine solution in acetic acid (1.14 g, 7 mmol, in 10 ml) was added over a period of 20 min to a solution of 4-chlorobenzyl cobaloxime in acetic acid (1.62 g, 3.3 mmol, in 15 ml) in the dark, under nitrogen. The progress of the reaction was monitored by TLC on silica gel using ethyl acetate as the eluent. On completion, the inorganic product was filtered off and the mixture was poured into water (50 ml). The organic product was extracted with an ether solvent. The organic layer was neutralized with sodium bicarbonate (concentration 5%) followed by water and sodium metabisulphite. Dichloromethane extraction of the aqueous part produced more inorganic bromocobaloxime(III). The ethereal layer, on evaporation, resulted in the organic product which was further separated and purified on the preparative silica gel plate using dichloromethane as solvent.

Reaction of 4-Nitrobenzyl Cobaloxime with Lithium Halide

A mixture of 4-nitrobenzylcobaloxime (1.00 g, 2 mmol) and lithium chloride (1.68 g, 4 mmol) in $CHCl_3$ (30 ml) was heated on a steam bath at 60 °C. A slow stream of oxygen was bubbled through the mixture. After 3 h, the mixture was poured on a silica gel column and eluted with CH_2Cl_2. The organic product was further separated on the preparative silica gel TLC plate by elution with CH_2Cl_2:pentane (1:1).

Physical Measurements and Instruments

^1H NMR spectra were recorded on a Varian HA-100 at room temperature. Elemental and mass spectral analyses were carried out at The Regional Sophisticated Instruments Centre, Lucknow. The UV–Vis absorption spectra were recorded on a Cary 17-D spectrophotometer at ambient temperature.

Results

All the reactions were carried out in chloroform or acetic acid, at room temperature, in the dark, under nitrogen with 1 mol of excess halogen (Cl_2 or Br_2). Within the reaction time scale, none of the organocobaloximes showed any sign of decomposition in the absence of halogens. All the organic halides

*For Part I, see ref. 3b.

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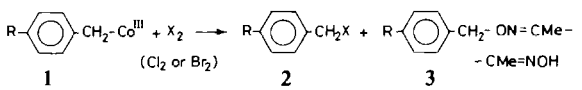
TABLE I. Products of Reaction of Halogens with Benzylcobaloximes in Acetic Acid



1 2 3

1	2	3
a R=H	a R=H; X=Br	a R=H
b R=Cl	b R=H; X=Cl	b R=Cl
c R=Br	c R=Cl; X=Br	c R=Br
d R=CHO	d R=Cl; X=Cl	d R=CHO
e R=CN	e R=Br; X=Br	e R=CN
f $R=NO_2$	f R=Br; X=Cl	f $R=NO_2$
g $R=CH_3$	g R=CHO; X=Br	
h $R=CH(CH_3)_2$	h R=CHO; X=Cl	
i $R=C(CH_3)_3$	i R=CN; X=Br	
	j R=CN; X=Cl	
	k $R=NO_2$; X=Br	
	l $R=NO_2$; X=Cl	
	m $R=CH_3$; X=Br	
	n $R=CH_3$; X=Cl	
	o $R=CH(CH_3)_2$; X=Br	
	p $R=CH(CH_3)_2$; X=Cl	
	q $R=C(CH_3)_3$; X=Br	
	r $R=C(CH_3)_3$; X=Cl	

Substrate (1 mol)	Halogen (2 mol)	Organic product[a]	
1a	Br_2	2a	(≥90%)
	Cl_2	2b	(62%), 3a (38%)
1b	Br_2	2c	(≥92%)
	Cl_2	2d	(65%), 3b (35%)
1c	Br_2	2e	(≥90%)
	Cl_2	2f	(72%), 3c (28%)
1d	Br_2	2g	(90%), 3d (8%)
	Cl_2	2h	(62%), 3d (38%)
1e	Br_2	2i	(90%), 3e (10%)
	Cl_2	2j	(64%), 3e (36%)
1f	Br_2	2k	(80%), 3f (20%)
	Cl_2	2l	(55%), 3f (40%)
1g	Br_2	2m	(≥90%)
	Cl_2	2n	(≥95%)
1h	Br_2	2o	(≥92%)
	Cl_2	2p	(≥95%)
1i	Br_2	2q	(≥95%)
	Cl_2	2r	(≥95%)

[a]Based on NMR spectra and GLC. [b]From ref. 3a.

obtained were known and, therefore, were identified by the NMR spectra using the authentic samples. Beside organic halides, varying amounts of the corresponding benzyl–ether of dimethylglyoxime (**3a–f**) were isolated in each reaction (see Table I). The ^1H NMR spectra and other characteristics of these products are given in Table II.

Chlorination of *p*-nitrobenzylcobaloxime (**1f**) in acetic acid was carried out in the presence of 1 mol of bromide ion (added as $(CH_3)_4NBr$). The organic product was isolated and identified by NMR as a mixture of *p*-nitrobenzyl bromide (**2k**) and *p*-nitrobenzyl chloride (**2l**). The comparative yield of *p*-nitrobenzyl bromide was greater than the corresponding chloride when it was carried out in the presence of a large excess of bromide ion. However, the extent of the formation of **3f** was lowered. Bromination in the presence of chloride ion gave similar results. Although chlorinations were more rapid than brominations in general, the change of solvent from chloroform to acetic acid did not lead to any significant change in the rate of reaction. The yields of the organic products were found to be better in chloroform than in acetic acid.

Discussion

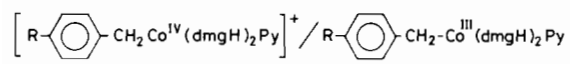
Chlorination of benzyl cobaloxime (**1a**) by molecular chlorine formed 38% benzyl ether of dimethylglyoxime (**3a**) as a by-product [3a]. No explanation was offered. However, in subsequent studies, the formation of this by-product was suggested as being the result of an oxidative dealkylation mechanism consisting of a nucleophilic displacement of cobalt from the organocobalt(IV) species formed *in situ* [2a]. This suggestion was later supported by Halpern *et al.* who also confirmed the existence of an organocobalt(IV) species, quite stable at a low temperature (−70 °C), and which undergo nucleophilic substitution with a variety of nucleophiles [4]. The stability of the organocobalt(IV) species has recently been reviewed by Volpin *et al.* [6]. The formation of similar mono ethers of dimethylglyoximes has also been shown to occur as a side reaction in a number of reactions between organocobaloximes and various electrophilic oxidising reagents [7]. Recently, Tauzher *et al.* preferred the electrophilic mechanism in their halogenation study of benzyl cobaloxime with ICl and ICl_2^-. They also made further generalisations, *i.e.* that other benzyl cobaloxime derivatives will also react via a similar mechanism [8] although they only studied benzyl cobaloxime. The formation of benzyl ethers of dimethylglyoximes (**3a–f**) and the formation of mixed halides when chlorinations are carried out in the presence of bromide ion, points to an oxidative dealkylation mechanism as follows. The extent of the formation of (**3a–f**) is greater in chlorination than in bromination. Since chlorine is a better oxidising agent than bromine, it will oxidise the complex fairly rapidly and completely, maybe before much nucleophilic displacement and ether formation takes place, whereas bromine may not oxidise the complex quite as completely. Since chloride ion is much weaker as a nucleophile than bromide ion, any competition between nucleophilic displacement (a second-order process) and ether formation (probably a first-order process) will favour the ether formation in the case of weaker chloride

TABLE II. Characteristics of Benzyl Ethers of Dimethylglyoxime

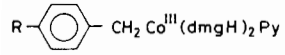
Compound	Melting point (°C)	^{1}H NMR: δ ($CDCl_3^3$) (TMS)			m/e	UV: λ (nm) (in CH_3OH)
		Aromatic	$-CH_2$	dmgH		
3a[a]	90–92	7.23	5.10	2.00	–	–
3b	98	7.20	5.16	1.90, 2.30	240	226
3c[b]	100	7.12, 7.32	5.14	1.90, 2.30	285, 283	220
3d[c]	93	7.52, 7.90	5.18	2.25, 2.28	234	236, 273
3e	95	7.40, 7.52	5.16	1.95, 2.04	231	235
3f[b]	99	7.50, 8.20	5.35	2.05, 2.35	251	217, 230, 260

[a]From ref. 3a. [b]Both isomers (*syn* and *anti*) are observed in ^{1}H NMR. [c]CHO appears at 10.0 δ.

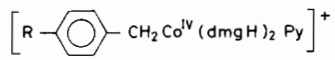
ion. The higher reactivity of chlorine as compared to bromine is as expected and is justified, keeping in view the similarities of the reduction potential of



and that of Br_2/Br^- ($E = 0.82$ V). It is quite likely that some



and Br_2 may be formed through the oxidation of Br^- by



However, the corresponding Cl_2/Cl^- potential is quite high ($E = 1.1$ V) so as to preclude oxidation of Cl^- to Cl_2 under the reaction conditions. Since the tendency of oxidation to organocobalt(IV) species decreases with the increase in the donor strength of the substituent in the benzene ring [4], the formation of benzyl halides alone, probably by direct electrophilic mechanism, in (**1g–i**) is not surprising.

The formation of mixed halides when chlorinations are carried out in the presence of bromide ion and the lower proportion of monoethers of dimethylglyoxime when this was done in the presence of a large excess of bromide ion can be explained as follows. Chlorine being a better oxidant, apart from oxidising the cobaloxime, it will react with bromide ion to give Cl^- and BrCl. In the presence of more bromide ion it will form Cl^- and Br_2. This is, therefore, merely changing the halogen, progressively making it Cl_2, BrCl and Br_2, thus a weaker oxidising agent. In the process, the amount of halide ion is increased, hence the decrease in the ether formation. The complete scheme can be written as follows.

$$ArCH_2Co^{III}(dmgH)_2Py + X_2 \longrightarrow ArCH_2Co^{IV}(dmgH)_2Py^+ + X_2^{\cdot-} \quad (1)$$

$$X_2^{\cdot-} \longrightarrow \bar{X} + \dot{X} \quad (2)$$

$$ArCH_2Co^{III}(dmgH)_2Py + \dot{X} \longrightarrow ArCH_2Co^{IV}(dmgH)_2Py^+ + \bar{X} \quad (3)$$

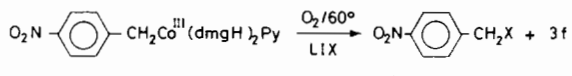
$$ArCH_2Co^{IV}(dmgH)_2Py^+ + X^- \longrightarrow ArCH_2X + Co^{II}(dmgH)_2Py \quad (4)$$

$$Co^{II}(dmgH)_2Py + X_2 \longrightarrow XCo^{III}(dmgH)_2Py + X^- \quad (5)$$

$$\dot{X} + Co^{II}(dmgH)_2Py \longrightarrow XCo^{III}(dmgH)_2Py \quad (6)$$

$RCo^{III}(dmgH)_2Py$ is oxidised to $RCo^{IV}(dmgH)_2Py^+$ and the other product formed in this oxidation process is $X_2^{\cdot-}$ (eqn. 1), which must break down to X^- and $\dot{X}$ (eqn. 2). The fate of X^- has been discussed above, however $\dot{X}$ can do several things including oxidising more $RCo^{III}(dmgH)_2Py$ to $RCo^{IV}(dmgH)_2Py^+$ (eqn. 3) or act as a displacing radical. Equation 5 will occur only if $Co^{II}(dmgH)_2Py$ is formed in the presence of excess X_2. At this stage, we are not sure as to what really happens to the radicals but it is certain that the halogenation of cobaloximes seems to proceed with a complicated reaction mechanism.

The following result provides further support for the above oxidative dealkylation mechanism since *p*-nitrobenzyl halide can only come about by a nucleophilic attack on the oxidised organocobalt(IV) species formed *in situ*.



It appears that our results point to an oxidative dealkylation mechanism and do not conform with the generalisation made by Tauzher *et al.* The results further indicate that even a small difference in the oxidation potential realized on varying the substituent in the benzene ring is sufficient to cause a change of mechanism from electrophilic (R = Me,

isopropyl t-Bu) to oxidative dealkylation mechanism (R = H, Cl, Br, CHO, CN, NO_2). Moreover, it seems certain that the oxidative dealkylation process initiates the free radical mechanism in solution as well.

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