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Oxidation of Benzyl Cobaloximes by Manganese(III) Acetate

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Abstract

Oxidation of benzyl cobaloximes by Mn(III) acetate leads to the formation of benzyl ethers of dimethylglyoxime.

Introduction

Homolytic displacement of a radical $\dot{Y}$ from a saturated carbon by another radical $\dot{X}$, the S_H2 reaction (eqn. (1)), is of immense importance in synthetic organic chemistry.

$$\dot{X} + RCH_2Y \longrightarrow RCH_2X + \dot{Y} \qquad (1)$$

Recently a number of papers have described a series of novel homolytic reactions between a free radical precursor and diamagnetic σ-bonded organometallic complexes [1]. In all these reactions, the key step involved is the homolytic displacement of a paramagnetic, low-valent, metal complex by an attack of a C or S centred radical on the organic ligands of the organometallic complex.

$$RCo^{III}(dmgH)_2B + \dot{X} \longrightarrow RX + Co^{II}(dmgH)_2B$$

R = allyl, allenyl, butenyl, alkyl, benzyl etc.

$\dot{X} = \dot{C}Cl_3, \dot{C}Cl_2CN, \dot{C}Br_3, Ph\dot{S}, R\dot{S}O_2$ etc.

Manganese(III) acetate has been shown to be a good source of $\dot{C}H_2COOH$ radicals when heated at 150 °C [2]. Since there are very few examples of the homolytic attack at a saturated carbon centre [3], it seemed worthwhile to try to prepare substituted acetic acids, RCH_2COOH, by a S_H2 reaction between this radical and benzylcobaloximes.

In this paper, we report that the reaction of Mn(III) acetate with benzyl cobaloximes at 150 °C does not lead to the anticipated products; instead, benzyl ethers of dimethylglyoxime are the exclusive organic products.

Experimental

Benzyl cobaloximes were prepared by the literature procedure 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 [4].

Reaction of Manganese(III) Acetate with Benzylcobaloximes

In a typical experiment, a solution of 1f (500 mg, 1.03 mmol), Mn(III) acetate (600 mg, 2.2 mmol), sodium acetate (500 mg, 6.1 mmol) in 15–20 ml of glacial acetic acid and 3 ml of acetic anhydride was heated to 150 °C. The progress of the reaction, which took less than 90 min in all cases, was monitored by TLC on silica gel using ethyl acetate as the eluent. The reaction was worked up by addition of water and then extraction with solvent ether. The product was obtained as a white solid (73%) and was further recrystallised from petroleum ether*.

Physical Measurements and Instruments

^{1}H NMR spectra were measured on a Varian HA100 at room temperature. UV–Vis absorption spectra were recorded on a Cary 17-D spectrophotometer at ambient temperature. Melting points were taken on Fischer–Jones melting point apparatus. The elemental and mass spectral studies were carried out at Regional Sophisticated Instruments Centre, Lucknow.

Results and Discussion

All the reactions were carried out in glacial acetic at 150 °C. A single organic product, identified by

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*Two isomers were observed in some cases (see Table I). The separation proved to be very difficult. However, compound **III** was separated on a preparative TLC plate on silica gel using benzene/chloroform (1:1) as the eluents. The major component (isomer **A**) has m.p. 105 °C and the minor (isomer **B**) has 75 °C. The yield, melting point and UV presented in Table I refer to the mixture data. However, the products gave satisfactory elemental analyses.

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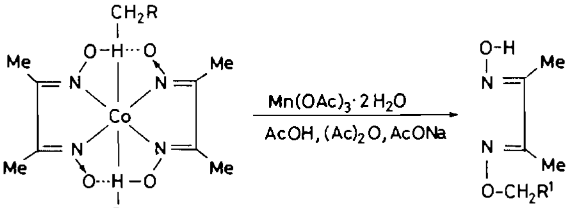
TABLE I. Characteristics of HON=C(Me)–C(Me)=NO–CH$_2$R (**IIa–m**)

Compound	Yield (%)	Melting point (℃)	^{1}H NMR: δ (CDCl$_3$) (TMS)			UV (CH$_3$OH) (nm)	Mass (m/e)[e]
			dmgH	–CH$_2$	Aromatic		
a[a]	38	90–92	1.95	5.10	7.23	–	–
b	52	98	1.90, 2.30	5.16	7.20	226	239(1.5%), 124(100%)
c	56	100	A 1.90, 2.30	5.14	7.12, 7.32	220	285(2%), 170(100%),
			B 2.22, 2.35	5.10	7.12, 7.32		283(2%), 168(100%)
d	32	99	A 2.05, 2.35	5.35	7.50, 8.20	217, 230,	250(60%), 135(100%)
			B 2.18, 2.22	5.10	7.50, 8.20	260	
e[b]	50	93	2.25, 2.28	5.18	7.52, 7.90	236, 273	234(6%), 119(98%)
f	73	95	1.95, 2.04	5.16	7.40, 7.52	235	231(10%), 116(100%)
g	45	85	2.00, 2.08	5.12	7.16	228	220(2%), 105(100%)
h	33	65	A 2.30, 2.33	5.28	7.50, 8.14	222	251(12%), 136(50%)
			B 2.06, 2.14	5.16	7.50, 8.14		
i	43	99	2.22, 2.30	5.15	7.35	222	–
j	42	101	A 2.24, 2.28	5.54	7.26, 7.40	312	239(2%), 122(100%)
			B 2.08, 2.18	5.36	7.26, 7.40		
k	40	74	2.24, 2.27	5.20	7.30, 7.46	228	–
l	40	115	A 2.27, 2.30	5.64	7.40, 7.76, 8.02	223	256(0.5%), 141(100%)
			B 2.09, 2.16	5.52	7.40, 7.76, 8.02		
m	48	106	A 2.28, 2.32	5.14	6.40, 7.58	222	–
			B 2.18	5.27	6.40, 7.58		

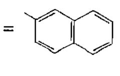
[a] From ref. 5b; [b] CHO appears at 10.0 δ; [c] values refer to M$^+$, (M–dmgH)$^+$ but for **IIb** and **d**, the values refer to (M–H)$^+$ and (M–H–dmgH)$^+$ and for **j** it refers to (M + H)$^+$ and (M–H–dmgH)$^+$.

^{1}H NMR as benzyl ether of dimethyl glyoxime, was obtained in each case. The same reactions under nitrogen atmosphere and at lower temperature (80–90 ℃) did not lead to a change of product. However, the yield was drastically lowered (⩽20%) when the reaction took place in the absence of acetic anhydride. The yield of the organic product varied with the R group. The ^{1}H NMR spectra as well as some other characteristics of these products are given in Table I.

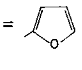
The formation of *o*-organodimethylglyoxime monoethers (R = allyl, allenyl) has been observed as a side product in many electrophilic and free radical reactions of cobaloximes [1d, 5, 6b]. Except for **IIa**, which has been characterised by various workers [5], no other product has been mentioned earlier. The exclusive formation of these products indicates that the homolytic substitution by $-\dot{C}H_2COOH$ radicals does not occur; instead, the reaction probably involves the intermediate formation of a radical cation $RCo(dmgH)_2Py^{\dot{+}}$ by one-electron oxidation. The existence of this species has been confirmed by Halpern *et al.* in their oxidation study of benzyl(aquo) cobaloxime by $IrCl_6^{2-}$ [7]. The recent detailed study of the stoichiometry, kinetics and stereochemistry of reactions of organo cobalt chelates with halogens and interhalide compounds indicates that most of these processes involve cobalt-(IV) species [6, 8]. The stability of organo cobalt(IV) species has recently been reviewed by Volpin *et al.* [9]. The radical cation is very unstable at higher temperatures and undergoes intramolecular transfer of the organic group to the equatorial ligand.



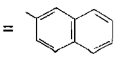
a, R = $-C_6H_5$
b, R = $-C_6H_4$-*p*-Cl
c, R = $-C_6H_4$-*p*-Br
d, R = $-C_6H_4$-*p*-NO$_2$
e, R = $-C_6H_4$-*p*-CHO
f, R = $-C_6H_4$-*p*-CN
g, R = $-C_6H_4$-*p*-Me
h, R = $-C_6H_4$-*m*-NO$_2$
i, R = $-O-C_6H_5$
j, R = $-S-C_6H_5$
k, R = $-NH-C_6H_5$
l, R =



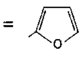
m, R =



a, R^1 = $-C_6H_5$
b, R^1 = $-C_6H_4$-*p*-Cl
c, R^1 = $-C_6H_4$-*p*-Br
d, R^1 = $-C_6H_4$-*p*-NO$_2$
e, R^1 = $-C_6H_4$-*p*-CHO
f, R^1 = $-C_6H_4$-*p*-CN
g, R^1 = $-C_6H_4$-*p*-Me
h, R^1 = $-C_6H_4$-*m*-NO$_2$
i, R^1 = $-O-C_6H_5$
j, R^1 = $-S-C_6H_5$
k, R^1 = $-NH-C_6H_5$
l, R^1 =



m, R^1 =



This transfer may occur either as a nucleophilic displacement of cobalt(IV) by the dimethylglyoxime anion (S_N2') or as a homolytic displacement of cobaloxime(III) by the dimethylglyoxime radical (S_H2'). It is very difficult to distinguish between these two processes. However, the S_H2' mechanism has been preferred by earlier workers [3, 5].

The exclusive formation of dimethylglyoxime mono-ethers is surprising since the nucleophilic substitution by the CH_3COO^- ion at the organocobalt(IV) species is expected to form benzylic acetates. Since CH_3COO^- ion is much weaker as a nucleophile; hence, any competition between nucleophilic displacement (a second order process) and ether formation (probably a first order process) will favour the formation of dimethylglyoxime monoether. We have made similar observations in the halogenation of benzylcobaloximes [6b]. These reactions are of considerable importance in view of their possible role as steps in the halogen cleavage of the metal–carbon bond [6].

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