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Halogenolysis of Benzylcobaloximes (1)

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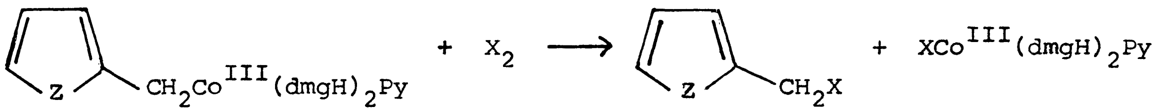
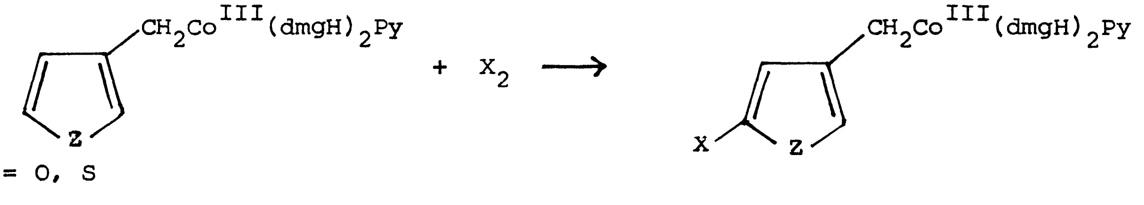
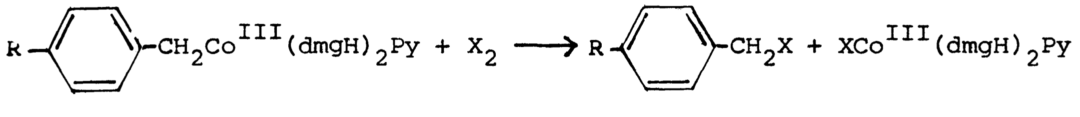
The reaction of substituted benzylcobaloximes p-$RC_6H_4CH_2Co(dmgH)_2$-Py (R = OMe, $NHCOCH_3$ and NMe_2) and m-$RC_6H_4CH_2Co(dmgH)_2Py$ (R = Me, OMe) with halogens (Cl_2 and Br_2) in chloroform under nitrogen forms ring substituted organic and organometallic products.

Several organometallic cobalt(III) complexes, RCo(salen), RCo(acacen), $RCo(dmgH)_2B$ are known to react with halogens.(2) The study is important in view of the many proposed mechanisms. Halogenation of benzylcobaloximes is particularly interesting since direct competition between ring halogenation and Co-C bond cleavage has been observed.(2,3) While Co-C bond cleavage is the primary process in the halogenation of 2-furyl and 2-thienyl methyl cobaloximes, halogenation of the heterocyclic ring occurs more rapidly in 3-furyl and 3-thienyl methyl cobaloxime. Since halogenations are among those reactions whose rates are most susceptible to nature, position and number of substituents in the aromatic ring, the tendency of ring substitution should increase if the aromatic ring is supplemented with activating groups. We have recently shown that the substitution of methyl, isopropyl and t-butyl groups in the para-position of benzylcobaloxime is not sufficient enough to overcome the high rate of side chain Co-C cleavage.(5) It is possible that in these systems the competitive cleavage of Co-C bond has also been effected by these activating groups.





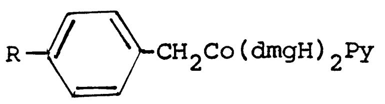
Z = O, S



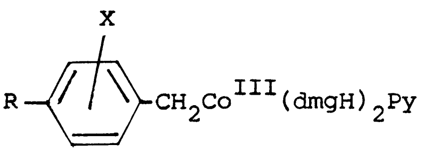
R = H; Me; $CHMe_2$; CMe_3
X = Cl_2; Br_2

Since the influence of the conjugatively electron releasing groups on the ring substitution is much more than their influence on the side chain reactions as shown by the much greater values of brown σ+ constants than the Hammett σ constants for such substituents and by the larger values of ρ for such substitution reactions, the side chain Co-C cleavage should, therefore, not be greatly effected by these substituents.$^{6)}$ We demonstrate here that the substitution of conjugatively electron releasing groups in the benzylcobaloximes leads to the halogenation of the aromatic ring.

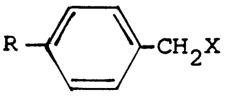
Benzylcobaloxime 1 or 2 (1 mmol in 15 ml chloroform) react with one or two moles of halogens (Cl_2 and Br_2) in 10 ml of dry chloroform at room temperature under nitrogen atmosphere. The reactions are done under conditions where the concentration of halogen is kept as low as possible and the reactions of higher order in halogens are negligible. Both organic and organometallic compounds are formed in varying proportions indicating that the substitution in the aromatic ring is accompanied by a competing Co-C bond cleavage (Table 1).



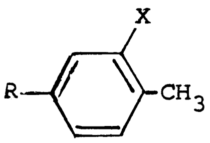
1, R = NMe_2
2, R = $NHCOCH_3$
3, R = OMe



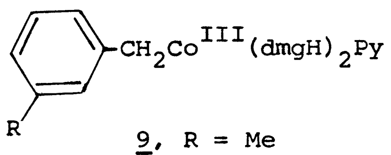
4, R = NMe_2; X = Cl or Br
5, R = $NHCOCH_3$; X = Cl or Br



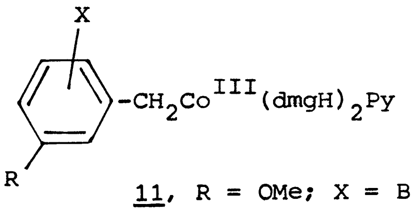
6, R = NMe_2; X = Cl
7, R = $NHCOCH_3$;
X = Cl or Br



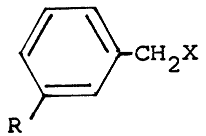
8, R = OMe; X = Cl
or Br



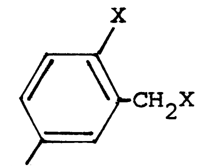
9, R = Me
10, R = OMe



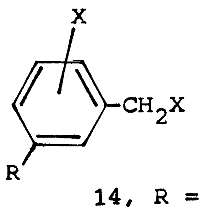
11, R = OMe; X = Br



12, R = Me; X = Br



13, R = Me; X = Br



14, R = OMe; X = Br

Table 1. Products of reactions of halogen with benzylcobaloximes

Substrate	Halogen (mol)	Organometallic product[a)]	Organic product[a)]
1	Br_2 (1 or 2)	4 (100%)	None
	Cl_2 (1)	4 (67%)	6 (33%)
	Cl_2 (2)	4 (60%)	6 (40%)
2	Br_2 (1)	5 (44%)	7 (56%)
	Br_2 (2)	5 (35%)	7 (65%)
	Cl_2 (1)	5 (30%)	7 (70%)
	Cl_2 (2)	5 (25%)	7 (75%)
3	Br_2 (1 or 2)	None	8 (100%)
	Cl_2 (1 or 2)	None	8 (100%)
9	Br_2 (2)	None	12 (50%) 13 (50%)
10	Br_2 (1)	11 (40%)[b)]	14 (60%)[b)]
11[b]	Br_2 (1)	None	14 (100%)[b)]

a) Isolated yield in parenthesis.
b) Each is a mixture of two positional isomers (65:35)

4-N,N-Dimethyl benzyl chloride 6, a Co-C bond cleavage product is highly unstable and is isolated and characterised by its reaction with thiophenol. Owing to the very compact nature of aromatic proton resonances in 4 and 5, the position of halogen is very difficult to assign[7)] though the complexes 4 and 5 are pure with single isomer only. The exclusive formation of 8 and the complete absence of other isomer where halogen is ortho to methoxy group points to the more activating effect of $CH_2Co^{III}(dmgH)_2B$ group than methoxy. The product 8 is formed probably by the attack of halogen on the ring with a concerted cleavage of the Co-C bond. The possibility that bromination initially takes place without cleavage and then the HBr present may cleave the Co-benzyl bond is ruled out, since the reaction of 3 with pure HBr in chloroform under identical conditions is very slow (4 days) and does not form any p-methoxytoluene.

The substitution in the meta-position seems to be much more effective in causing the ring substitution, for example, in the bromination of 9, 50% reaction involves an initial attack of bromine on the ring followed by Co-C bond cleavage and 50% reaction involves direct Co-C bond cleavage prior to ring substitution. meta-Methylbenzyl bromide is inert to such bromination under similar conditions. meta-Methoxybenzylcobaloxime 10, on the other hand, forms initially the ring substituted organometallic product 11, a part of which undergoes Co-C cleavage to form 14.

Interestingly, the protonation of the equatorial dimethylglyoximato ligand changes the course of reaction, for example, p-methylbenzyl bromide is the exclusive product in the bromination of p-methylbenzyl cobaloxime5) whereas the latter in the presence of 20% H_2SO_4 forms substantial amounts (≈90%) of p-methylbenzyl ether of dimethylglyoxime, a characteristic decomposition product of organocobalt(IV) species.9) Only very little amount (10%) of p-methylbenzyl bromide is formed. Halogenation studies on cobaloximes of the type $PhXCH_2$-$Co^{III}(dmgH)_2Py$ (X = O, S, NH) are being done in our laboratory. The preliminary results indicate that both Co-C cleavage and ring substitution occur simultaneously.

References

1) Part III. For part II, see Ref. 5.

2) F.R. Jensen, V. Madan, and D.H. Buchanan, J. Am. Chem. Soc., 93, 5283 (1971); D. Dodd and M.D. Johnson, J. Organomet. Chem., 52, 1 (1973); R.D.W. Kimmett and D.R. Russel, "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, Pergamon, Oxford (1982), Vol. 5, pp. 106-113, M.D. Johnson, Acc. Chem. Res., 11, 57 (1978); J. Halpern, Angew. Chem., Int. Ed. Engl., 24, 274 (1985); M.D. Johnson, "The Chemistry of Metal Carbon Bond," ed by F.R. Hartley and S. Patai, John Wiley (1985), Vol. 2, pp. 513-554.

3) S.N. Anderson, D.H. Ballard, and M.D. Johnson, J. Chem. Soc., Perkin Trans. 2, 1972, 311.

4) B.D. Gupta and S. Roy, Tetrahedron Lett., 25, 3255 (1984).

5) B.D. Gupta and M. Kumar, Inorg. Chim. Acta, 113, 9 (1986) and references cited therein.

6) H.C. Brown and Y. Okamoto, J. Am. Chem. Soc., 80, 4979 (1958).

7) All compounds are characterised from their ^1H NMR spectra, elemental analysis and by comparison with the authentic samples wherever possible.

8) The synthesis of 8 in quantitative yield by this procedure may become valuable since other methods of preparation are lengthy and low yielding, e.g., M.S. Carpenter and W.H. Easter, J. Org. Chem., 20, 401 (1955).

9) M. Roy, M. Kumar, and B.D. Gupta, Inorg. Chim. Acta, 114, 87 (1986).

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