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HALOGENATION OF THENYL AND FURYL COBALOXIMES

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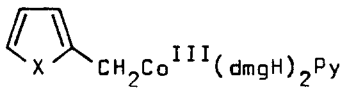
Summary. The reactions of thenyl and furyl cobaloximes with halogens (bromine and chlorine) in acetic acid and chloroform indicate that, Co-C bond cleavage occurs in 2-thenyl and 2-furyl case whereas the ring substitution is faster than Co-C bond cleavage in 3-thenyl and 3-furyl cobaloximes.

The study of the cleavage of the Co-C bond by halogens in organometallic compounds of cobalt(III) has been of great interest and many papers giving different mechanisms have appeared in the recent past.[1] A direct competition between ring halogenation and cleavage of Co-C bond is pointed out by Johnson and coworkers. However, the activating influence of $-CH_2Co(dmgH)_2py$ is not sufficient on its own to overcome the high rate of sidechain cleavage of the Co-C bond in benzyl cobaloxime.[2] Ring substitution might, therefore, occur if the activation of the ring is increased some way. We have observed that substitution of conjugatively electron releasing groups in the para-position in benzyl cobaloximes leads to the ring substitution.[3] Since five membered heterocyclic ring compounds are, in general, more susceptible to electrophilic substitution, we demonstrate here, that such an observation is clearly visible in our study of the halogenation of 2- and 3- thenyl and furyl cobaloximes with bromine and chlorine.

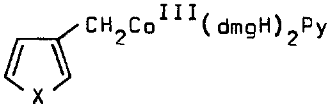
2- and 3- thenyl and furyl cobaloximes 1-4 rapidly react with 1 or 2 mole of halogen (Br_2 or Cl_2) in acetic acid or chloroform in dark at room temperature under nitrogen atmosphere. The reactions are done under condition where the concentration of halogen is kept as low as possible and the reactions of higher order in halogen are negligible. In 2-isomer, the Co-C bond cleavage occurs much faster and leads to the formation of the corresponding halides 5-8 which are unstable and are isolated and characterised as their adducts with hexamine (7 & 8) and as furfuryl ethers (5 & 6). However, the ring halogenation occurs much faster in 3-thenyl and 3-furyl cobaloximes leading to the formation of corresponding 5-substituted organometallic compounds 9-12. Interestingly, further cleavage of Co-C bond occurs with excess halogen resulting in the formation of 13-16.[4] The exclusive formation of 5-substituted organometallic products and the complete absence of 2-substituted products points to the steric crowding by the bulkier $-CH_2Co^{III}(dmgH)_2py$ in the 3-position. The various competitive bromination reactions of 3-thenyl cobaloxime 4 with benzyl cobaloxime and with 3-methyl thiophene indicate that, 4 is much more reactive than benzyl cobaloxime and the group

$-CH_2Co(dmgH)_2py$ is more activating than the methyl group.

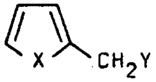
TABLE. Products of reactions of halogens with thenyl and furyl cobaloximes in acetic acid or chloroform in dark under nitrogen atmosphere



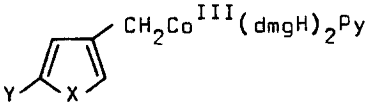
1, X = O
2, X = S



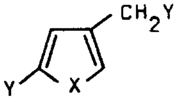
3, X = O
4, X = S



5, X = O; Y = Cl
6, X = O; Y = Br
7, X = S; Y = Cl
8, X = S; Y = Br



9, X = O; Y = Cl
10, X = O; Y = Br
11, X = S; Y = Cl
12, X = S; Y = Br



13, X = O; Y = Cl
14, X = O; Y = Br
15, X = S; Y = Cl
16, X = S; Y = Br

Substrate	Halogen (mole)	Organometallic* Product	Organic* Product
1	Cl_2 (1 or 2)	None	5
	Br_2 (1 or 2)	None	6
2	Cl_2 (1 or 2)	None	7
	Br_2 (1 or 2)	None	8
3	Cl_2 (1)	9	None
	Cl_2 (2)	None	13
	Br_2 (1)	10	None
	Br_2 (2)	None	14
4	Cl_2 (1)	11	None
	Cl_2 (2)	None	15
	Br_2 (1)	12	None
	Br_2 (2)	None	16

*Isolated in $\geqslant$ 90%

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1. a) F.R. Jensen, V. Madan and D.H. Buchnan, J. Am. Chem. Soc., 93, 5283 (1971); b) S.N. Andersen, D.H. Ballard, J.Z. Chrzastowski, D. Dodd, and M.D. Johnson, Chem. Comm., 685 (1972); c) D. Dodd and M.D. Johnson, J. Organometal. Chem., 52, 1 (1973); d) R. Dreos, G. Tauzher, N. Marsich and G. Costa, J. Organometal. Chem., 92, 227 (1975); e) R. Dreos Garlatti, G. Tauzher and G. Costa, J. Organometal. Chem., 182, 409 (1979).
2. S.N. Andersen, D.H. Ballard and M.D. Johnson, J. Chem. Soc. Perkin (II), 311 (1972).
3. B.D. Gupta and Manoj Kumar (unpublished results).
4. All compounds are characterised from their ^1H NMR spectra, elemental and halogen analysis as well as by comparison with the authentic samples wherever possible.

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