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REACTION OF COBALOXIME(I) WITH 2-ALLYLOXYETHYL HALIDES. EVIDENCE FOR AN ELECTRON TRANSFER MECHANISM

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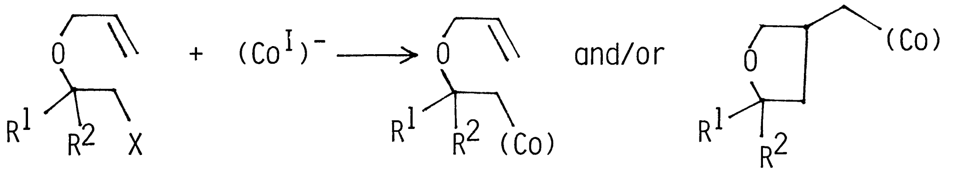
Reaction of Cobaloxime(I), $(Co^{I})^{-}$, with 2-allyloxyethyl halides (1, 2, and 3) gave cyclized organocobaloximes (5) formed by intramolecular rearrangement of 2-allyloxyethyl radicals to (3-tetrahydrofuranyl)methyl radicals. The intermediate radical must be formed by an electron transfer process which competes with an S_N2 reaction to give a non-cyclized organocobaloximes.

The reaction of bis-dimethylglyoximato(pyridine)cobalt(I) (hereafter cobaloxime(I) or $(Co^{I})^{-}$) with alkyl halides has been reported to take an S_N2 process by Schrauzer and Deutsch,(1) and Jensen *et al.*(2) Recently, however, Schaffler and Rétey claimed the possibility of an electron transfer mechanism without rigorous evidence for this class of reaction.(3) Now we like to report the reality of the latter mechanism. We used the cyclization of 2-allyloxyethyl radicals to (3-tetrahydrofuranyl)methyl radicals as a probe of radical intermediate (R·) formed by the separation of halide anion (X^{-}) from the radical anion $(RX^{\cdot-})$ (eq. 1).

$$(Co^{I})^{-} + R\text{-}X \longrightarrow (Co^{II}) + R\text{-}X^{\cdot-} \longrightarrow (Co^{II}) + R^{\cdot} + X^{-} \longrightarrow (Co^{III})R + X^{-} \qquad \text{---------(eq. 1)}$$

One of the 2-allyloxyethyl tosylates or 2-allyloxyethyl halides (1 mmol) was added under nitrogen to the methanol solution (3 ml) of cobaloxime(I)(4) (1 mmol) prepared *in situ* from cobalt(II) chloride, dimethylglyoxime, pyridine, and sodium borohydride, and the reaction mixture was stirred for 4 - 6 h. 2-Allyloxyethyl tosylate (1a) gave a direct substitution product, 2-allyloxyethylcobaloxime (4a),(5) but 2-allyloxy-2-phenylethyl tosylate (2a) did not show the reactivity toward cobaloxime(I). The cobaloxime(I) anion reacted with 2-allyloxyethyl bromide (1b) and its derivatives (2b, 3) to give the direct substitution product (4a) and/or

(3-tetrahydrofuranyl)methyl cobaloxime (5a) and its derivatives (5b, 5c). 2-Allyloxyethyl iodides (1c, 2c) have better reactivity than the corresponding tosylates (1a, 2a) and bromides (1b, 2b). 2,2-Diphenyl-2-(2-methyl-2-propenyloxy)ethyl bromide (6) gave both non-cyclized and cyclized organocobaloximes (7, 8).

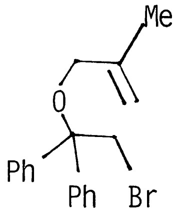


1a,b,c
2a,b,c
3

4a,b,c

5a,b,c

------(eq. 2)



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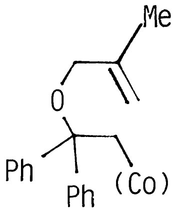

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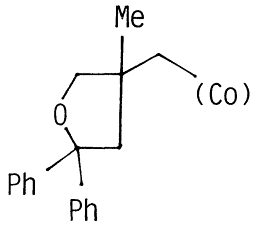

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Table 1. REACTION OF COBALOXIME(I) ANION, $(\mathrm{Co^{I}})^{-}$, IN METHANOL

substrate	R^1	R^2	X	product composition			yield (%)
				(4a)	:	(5a)	
1a	H	H	OTs	100		0	47
1b	H	H	Br	71		29	60
1c	H	H	I	35		65	66
				(4b)	:	(5b)	
2a	Ph	H	OTs	--		--	0
2b	Ph	H	Br	0		100	38
2c	Ph	H	I	0		100	55
				(4c)	:	(5c)	
3	Ph	Ph	Br	0		100	40
				(7)	:	(8)	
6	-	-	-	35		65	55

The formation of cyclized organocobaloximes (5a,b,c, and 8) suggests the intervention of 2-allyloxyethyl radicals. Lack of a solvolysis product even in lower concentration of cobaloxime in methanol excludes a cation intermediate. The results clearly suggest the radical intermediate which must be formed by a single electron transfer followed by the loss of halide ion (see eq. 1). The radical intermediate in the reaction of bromide (2b) was further substantiated by the formation of 4-methyl-2-phenyltetrahydrofuran (9) and 4-methylene-2-phenyltetrahydrofuran (10) as minor products. Decrease of the solvent polarity (MeOH → EtOH) lowered the yield of cyclized product (5a) from bromide (1b), since electron transfer process is sensitive to solvent polarity (see Figure 1).

The reaction mechanism can be summarized by the scheme shown in eq. 3. 2-Allyoxyethyl halides (2b, 2c, 3) having substituent at β-position give only the cyclized organocobaloximes (5b or 5c) due to inhibition of the direct substitution by the steric interaction between the substituent and the equatorial ligand of cobaloxime. This steric hindrance must inhibit both S_N2 and the direct radical

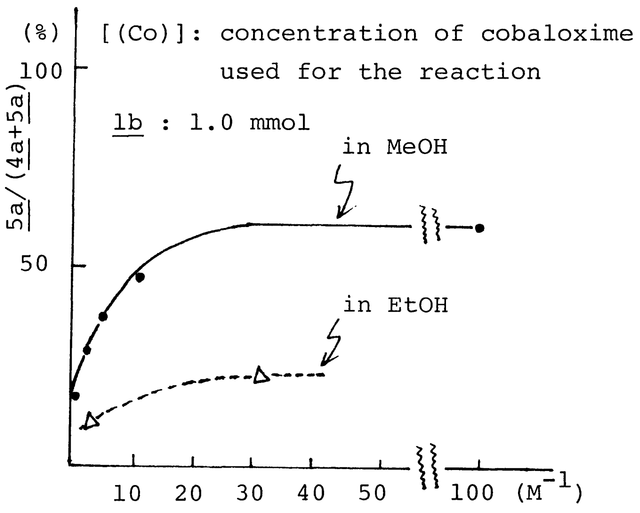
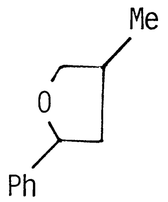


Figure 1. RELATION BETWEEN THE FORMATION OF 5a AND THE CONCENTRATION OF COBALOXIME.



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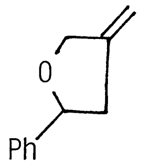

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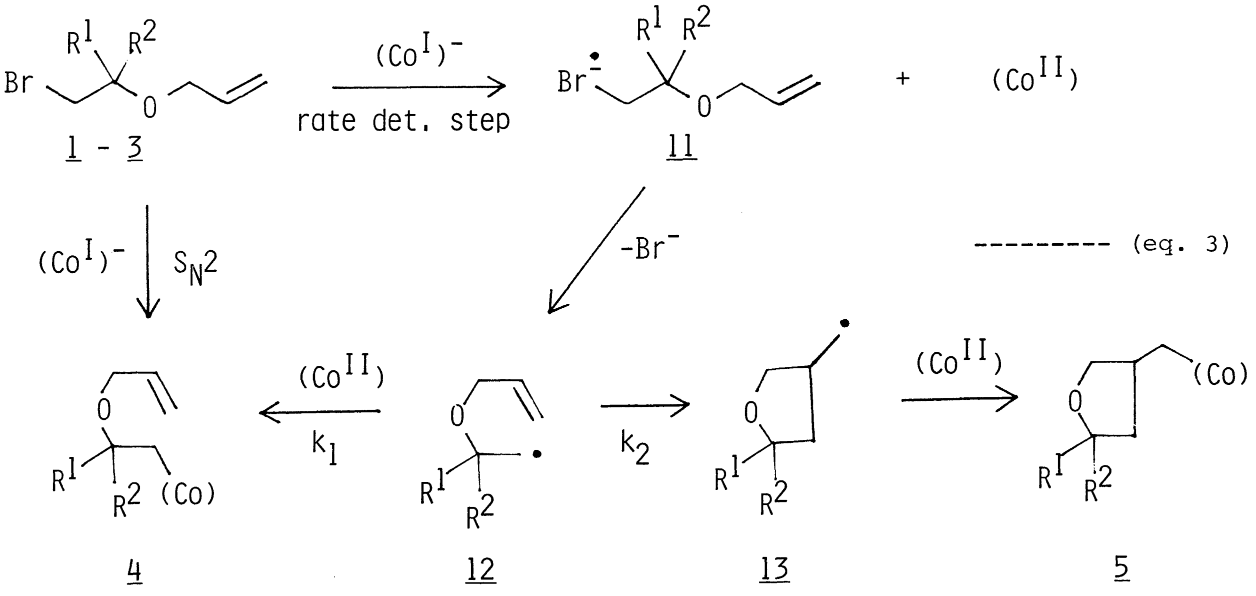

--------- (eq. 3)

coupling processes to give uncyclized organocobaloximes. Tosyl group is weak and hard leaving group and S_n2 reaction of tosylates with soft and bulky cobaloxime(I) must be sluggish. In the case of less hindered tosylate (1a) uncyclized organocobaloxime (4a) was obtained exclusively and it suggests the lack of the radical intermediate in the reaction of the tosylate. The formation of non-cyclized organocobaloxime (7) from 2,2-diphenyl-2-(2-methyl-2-propenyloxy)ethyl bromide (6) must be totally due to the electron transfer mechanism, since S_N2 mechanism is not operative with β-disubstituted halides such as (3). The substantial formation of non-cyclized organocobaloxime (7) from bromide (6), in contrast to the case of (3), must be due to the retardation of radical cyclization by methyl group at the reaction center.[6)]

The proportion of 4 and 5 from the radical intermediate (12), formed by electron transfer process, depends on the concentration of (Co^{II}) intermediate: $[4]/[5] = k_1[(Co^{II})]/k_2$. By carrying out the reaction in dilution method, we can decrease $[(Co^{II})]$ and retard the formation of 4. In high dilution state (total cobaloxime: 0.01 M), non-cyclized organocobaloxime (4) must be formed preferentially by S_N2 mechanism, 40% from 1b (see Figure 1). The radical coupling between the less hindered radical (12) and (Co^{II}) is substantial but the radical (12) having bulky substituent, from 2b, 2c, and 3, looses its reactivity to (Co^{II}) and only cyclized organocobaloximes (5b and 5c) were obtained.

These results support the reaction scheme shown in eq. 3 and prove that an electron transfer mechanism is more important than S_n2 mechanism for the reaction of cobaloxime(I) anion with bromides and iodides.

REFERENCES AND NOTE

1) G. N. Schrauzer and E. Deutsch, J. Am. Chem. Soc., 91, 3341 (1969).
2) F. R. Jensen, V. Madan, and D. H. Buchanan, J. Am. Chem. Soc., 92, 1414 (1970).
3) J. Schaffler and J. Rétey, Angew. Chem. Int. Ed.(English), 17, 845 (1978).
4) G. N. Schrauzer, Inorg. Synth., 11, 65 (1968).
5) All organocobaloximes obtained in this study gave correct elemental analyses and spectral data. The structures of the organocobaloximes were deduced from the photolysis products in the presence and absence of oxygen, and the transformation of the photolysis products to known compounds.
6) C. Walling and A. Cioffari, J. Am. Chem. Soc., 94, 6059 (1972).

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