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STEREOCHEMICAL STUDY ON THE REACTION OF COBALOXIME(I) WITH 2-SUBSTITUTED CYCLOHEXYL HALIDES. EVIDENCE FOR AN ELECTRON TRANSFER MECHANISM

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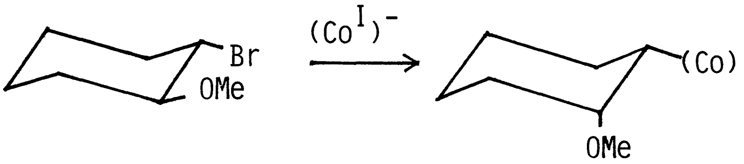
Reaction of cobaloxime(I), $(Co^{I})^{-}$, with 2-hydroxy- (1a and 1b) and 2-alkoxycyclohexyl halides (1c-1h) gave 2-hydroxy- and 2-alkoxycyclohexyl cobaloximes(III) (2 and 3). Stereochemistry of the organocobaloxime was independent of the configuration of the starting halides. 2-Allyloxycyclohexyl halides (6a and 6b) gave the organocobaloxime having 9-methyl-7-oxabicyclo[4,3,0]nonane moiety. These results show the radical intermediates formed by an electron transfer from cobaloxime(I) to the halides.

Jensen et al.[1)] have demonstrated that bis-dimethylglyoximato(pyridine)-cobalt(I), cobaloxime(I) or $(Co^{I})^{-}$, reacts with trans-2-methoxycyclohexyl bromide with inversion of configuration at the substitution center (Eq. 1).



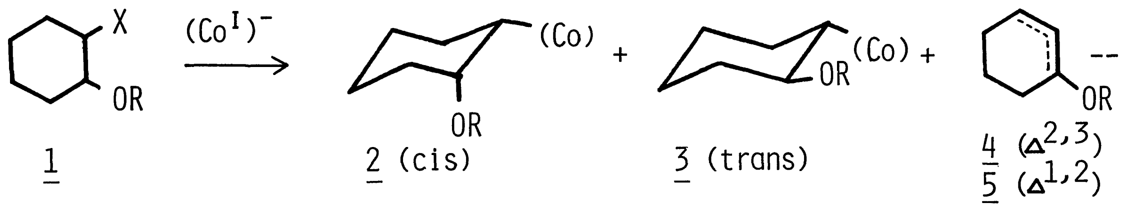
--- (Eq. 1)

This result seems to indicate that the reaction takes an S_N2 mechanism. However, we have presented that an electron transfer mechanism (Eq. 2) is more important

$$(Co^{I})^{-} + RX \longrightarrow (Co^{II}) + RX^{\bullet} \longrightarrow (Co^{II}) + R\bullet + X^{-} \longrightarrow$$
$$R\text{-}(Co^{III}) + X^{-} \qquad \text{----------------} \quad \text{(Eq. 2)}$$

than S_N2 mechanism in the reaction of cobaloxime(I) with 2-allyloxyethyl halides.[2)] Here we wish to report the stereochemical study on the reaction of cobaloxime(I) with 2-substituted cyclohexyl halides (1a-1h) and show that the reaction does not fit an S_N2 mechanism but matches with an electron transfer mechanism.

The reaction of cobaloxime(I)[3,4)] with 2-substituted cyclohexyl halides (1a-1h) in methanol gave cyclohexyl cobaloximes (2 and 3) (Eq. 3).[5)] The results



---(Eq.3)

Table 1. Reaction of cobaloxime(I) with cyclohexyl halides (1)

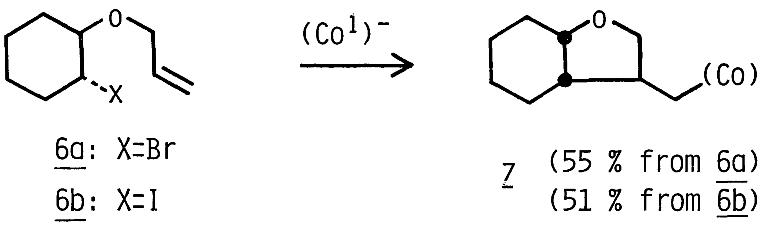
Starting halide	R	X	Stereo-chemistry	(2) : (3)[a)]	Yield(%)[b)]
1a	H	Br	cis	53 : 47	32
1b	H	Br	trans	55 : 45	11
1c	Me	Br	cis	100 : 0	17
1d	Me	Br	trans	100 : 0	18
1e	Me	I	cis	100 : 0	13
1f	Me	I	trans	100 : 0	19
1g	Pr	Br	trans	100 : 0	16
1h	Pr	I	trans	100 : 0	13

a) Ratio of 2 and 3 was determined by NMR analyses.

b) Isolated yield of organocobaloximes, (2 + 3).

are listed in Table 1. The reaction of cobaloxime(I) with 2-hydroxycyclohexyl bromides (1a and 1b) gave a mixture of cis- and trans-2-hydroxycyclohexyl cobaloximes (2 and 3, R=H). The ratio of 2 and 3 is independent on the configuration of the starting bromides. On the other hand, the reaction of cobaloxime(I) with 2-alkoxycyclohexyl halides (1c - 1h) gave only a cis-2-alkoxycyclohexyl cobaloxime (2, R=Me or Pr) regardless of the configuration of the starting halides. It is apparent that these results do not fit S_N2 mechanism and clearly show the existence of a common intermediate from the halides of either configuration.

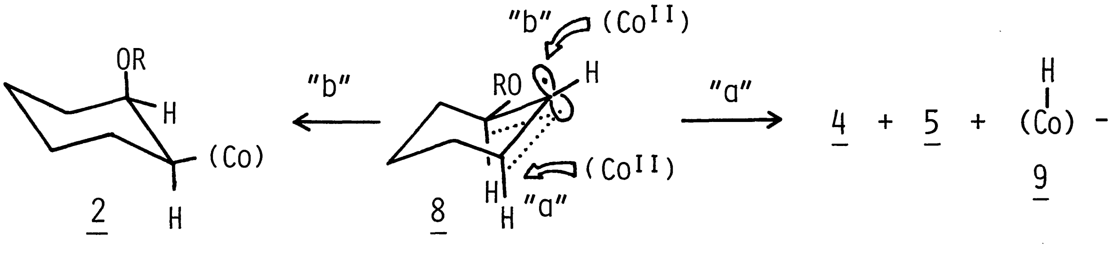
A major product was 3-propoxycyclohexene (4) on the reaction of cobaloxime(I) with halides (1g and 1h), 45 % from 1g. The product (4) could not be detected when these halides were treated under more basic conditions than those of the reaction with cobaloxime(I), and 2-propoxycyclohexylcobaloxime (2, R=Pr) gave no 4 under the present reaction conditions. The product (4), therefore, must be formed from the common intermediate to give organocobaloxime. In the case of halide (1d) we searched and found cyclohex-1-enyl propyl ether (5) in the products. After removal of the organocobaloxime, the product-mixture was treated with 2,4-dinitrophenylhydrazine to give a hydrazone of cyclohexanone, (5 % isolated yield), which is the hydrolysis product of 5. Low yield of the organocobaloximes (2 and 3) must be compensated by the formation of 4 and 5.



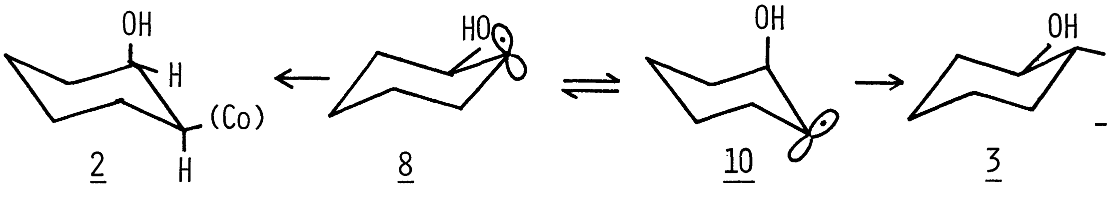
----- (Eq. 4)

The reaction of cobaloxime(I) with 2-allyloxycyclohexyl halides (6a and 6b) gave a cobaloxime (7) having 9-methyl-7-oxabicyclo[4,3,0]nonane group6) in reasonable yield (Eq. 4).7) Formation of this "cyclized organocobaloxime (7)" indicates the intervention of a radical intermediate, 2-allyloxycyclohexyl radical.2) The yield of organocobaloxime (7) is better than those of 2 and 3 and this is explained by the radical coupling between a primary radical and cobaloxime(II) in the former case. These results suggest that cobaloxime(I) reacts with cyclohexyl halides (1 and 6) by an electron transfer mechanism, in which the radical is formed by the electron transfer from cobaloxime(I) to halides followed by the release of halide ion from the radical anions (see Eq. 2).

The stereochemical course and the formation of olefin (4) and enol ether (5) on the reaction of cobaloxime(I) with halides (1a - 1h) can be understood by the following assumptions. First the 2-substituted cyclohexyl radical exists in a chair-like conformation. Second an alkoxy group takes an equatorial conformation. Third the carbon accommodating an unpaired electron takes an sp^2-like hybridization. This geometry of the intermediate radical (8) enables the p-orbital to overlap with the axial C-H bonds on the adjacent carbons8) by hyperconjugation. This effect should activate the axial hydrogens for the H-abstraction by (Co^{II}) (Eq. 5). If cobaloxime(II) approaches the radical (8) toward the bottom side (path "a" in Eq. 5), it should preferably abstract the activated axial hydrogen to



--- (Eq. 5)



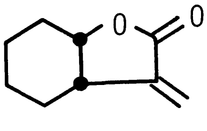
---(Eq. 6)

form 4 and 5, and hydrido-cobaloxime (9). By the approach toward the upper side (path "b"), it should couple to form cis-2-alkoxycyclohexyl cobaloxime (2) in spite of a severe steric hindrance since an activated hydrogen is not available on this side. In the case of 2-hydroxycyclohexyl bromides (1a and 1b), the hydroxy group may take an axial conformation (10) in a certain extent (Eq. 6) though we can not specify the reason, and this radical (10) is a conceivable precursor of trans-2-hydroxycyclohexyl cobaloxime (3). Thus the two conformations of the intermediate radical (8 and 10) must give the mixture of cis- and trans-2-hydroxycyclohexyl cobaloximes (2 and 3, Eq. 6).

In conclusion these results demonstrate that secondary halides with α-OH or OR group take an electron transfer mechanism as seen in primary halides[2)] and that an S_N2 mechanism claimed by Jensen et al[1)] is not operative in the cyclohexyl halides.

References and Notes

1) F. R. Jensen, V. Madan, and D. H. Buchanan, J. Am. Chem. Soc., 92, 1414 (1970).
2) M. Tada and M. Okabe, Chem. Lett., 1980, 201.
3) Cobaloxime(I) was prepared *in situ* from cobalt(II)chloride, dimethylglyoxime, pyridine, and sodium borohydride in methanol. See ref. 4.
4) G. N. Schrauzer, Inorg. Synth., 11, 65 (1968).
5) All organocobaloximes in this study gave correct elemental analyses and spectral data. The configuration of organocobaloximes was determined according to the method reported by Jensen *et al*.[1)]
6) The stereochemistry of 7 was determined by the transformation of the photolysis product to a known compound (11).[9)]
7) Compounds 12, 13, and 14 were also detected as minor products. They also indicate the existence of the radical intermediate.



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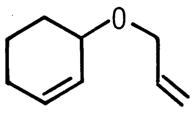

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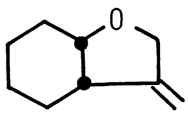

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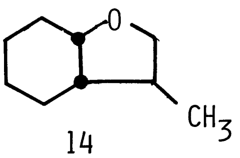

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8) A similar interaction has been reported in the enolization of cyclohexanone derivatives.[10)]
9) P. F. Hudrlik, J. M. Takacs, D. T-W. Chou, and L. R. Rudnick, J. Org. Chem., 44, 786 (1979).
10) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill Inc., New York (1962), p. 241.

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