taken from the linear portion of this plot; the data are given in Table I. Similar plots gave quantum yields for the other three products, for uncoordinated F^-, and for the disappearance of *trans*-$Cr(en)_2F_2^+$. These data are given in Table II, where the ion-exchange properties of the photoproducts are also presented. At the present time we have not firmly estabished the identity of the minor products; however, we have determined that *trans*-$Cr(en)_2H_2OF^{2+}$ is not one of these products. It is to be noted that within experimental error there is material balance in that the quantum yield for disappearance of *trans*-$Cr(en)_2F_2^+$ and the sum of the quantum yields for appearance of products are equal. Further, the data presented above indicate that a number of primary photoproducts can arise in photolysis of Cr(III) complexes; we note that, in general, only by a combination of ion-exchange *and* other techniques can the stoichiometry of such a photoprocess be resolved.

The data presented in Table II indicate that an upper limit on the amount of fluoride aquation in photolysis of *trans*-$Cr(en)_2F_2^+$ is about 17%. Clearly, Cr–N bond rupture is the predominant mode of photoaquation for *trans*-$Cr(en)_2F_2^+$ under our conditions. This conclusion is in agreement with the σ-bonding model, which predicts that absorption at 5200 Å populates the lowest lying σ-antibonding orbital, predominantly $d_{x^2-y^2}$ in character, and hence leads to stretching and ultimate rupture of a bond in the xy plane. In the prediction of the axis of labilization, the ligand-field strength approach often will parallel the σ-bonding model. A case in point is the photoaquation of *trans*-$Cr(en)_2Cl_2^+$ [5,18] which leads to loss of chloride, consistent with the predictions of either model.[19] However, our observations on *trans*-$Cr(en)_2F_2^+$ illustrate that in those critical cases in which the two models differ, the σ-bonding approach is superior.

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$(en)_2F_2^+$. For example, at 5200 Å, ϵ for *trans*-$Cr(en)_2F_2^+$ is 16.3 M^{-1} cm^{-1}, whereas ϵ for **1** is 40.0 M^{-1} cm^{-1}.

(18) L. Falk and R. G. Linck have independently verified the data reported in ref 5; ϕ for appearance of *cis*-$Cr(en)_2H_2OCl^{2+}$ is 0.35 at 6.5°.

(19) S. Yamada, *Coord. Chem. Rev.*, **2**, 83 (1967).

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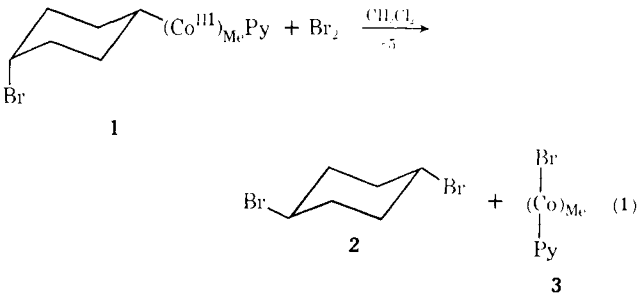
Halogen Cleavage of Carbon–Cobalt Bonds. Demonstration of Inversion at Carbon[1]

Sir:

Recent interest in the electrophilic cleavage of alkylcobalamins and cobaloximes[2–4] by mercuric salts and the implication of these or similar reactions in the production of organic mercury in the biosphere[4,5] prompted us to report our results on a closely related cleavage reaction. In this paper it is demonstrated that the cleavages of carbon–cobalt bonds by chlorine, bromine, and iodine all occur with *inversion* of configuration. In view of their general characteristics, these reactions are tentatively designated as electrophilic cleavages.

These results are also important in regard to the general question of the stereochemistry of SE2 reactions. Although it has been generally assumed that bimolecular electrophilic cleavage reactions occur with retention of configuration,[6] several reports of inversion have appeared.[7,8]

One equivalent of *cis*-4-bromocyclohexylcobaloxime (**1**)[9] was treated with 1.04 equiv of bromine in methylene chloride at −5° for 2 hr in the dark. All volatile materials were collected by high-vacuum transfer and concentrated by careful removal of the solvent through a fractionating column.



Gas chromatographic analysis revealed a 14% yield of *trans*-1,4-dibromocyclohexane (**2**) and an undetermined amount of cyclohexyl bromide. Coinjection of product **2** and authentic material[10] produced no new peaks. None of the isomeric *cis*-dibromide (**4**) was observed. Since under the conditions of the analysis[11] at least 3% of **4** could be detected in the presence of **2**, the cleavage of **1** by bromine occurs with at least 97% (100%, within experimental uncertainty) inversion of configuration at carbon. The solid residue left after removal of the volatile compounds from the reaction mixture was shown by chromatographic analysis to contain unreacted starting material, cobaloxime bromide (**3**), and some inorganic salt.

That these findings are not the result of some special characteristic of the cyclohexyl system was verified by cleavage of the optically active *sec*-butylcobaloxime (**5**) which also occurs with inversion at carbon. *sec*-Butyl alcohol, 43% optically pure,[12] was converted to the tosylate and allowed to react with the nucleophilic cobaloxime(I) as described previously.[9] The isolated

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(1) Presented by D. H. Buchanan at the Symposium on Bioinorganic Chemistry, Blacksburg, Va., June 24, 1970.

(2) H. A. O. Hill, J. M. Pratt, S. Ridsdale, F. R. Williams, and R. J. P. Williams, *Chem. Commun.*, 341 (1970).

(3) G. N. Schrauzer, J. H. Weber, T. M. Beckham, and R. K. Y. Ho, *Tetrahedron Lett.*, 275 (1971).

(4) N. Imura, E. Sukegawa, S. K. Pan, K. Nagao, J-Y. Kim, T. Kwan, and T. Ukita, *Science*, **172**, 1248 (1971).

(5) J. M. Wood, F. S. Kennedy, and C. G. Rosen, *Nature (London)*, **220**, 173 (1968).

(6) See, for example, R. W. Johnson and R. G. Pearson, *Chem. Commun.*, 986 (1970), and R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, **92**, 5519 (1970).

(7) (a) W. H. Glaze, C. M. Selman, A. L. Ball, Jr., and L. E. Bray, *J. Org. Chem.*, **34**, 641 (1969); (b) D. E. Applequist and G. W. Chmurny, *J. Amer. Chem. Soc.*, **89**, 875 (1967).

(8) (a) G. M. Whitesides and D. J. Boschetto, *ibid.*, **93**, 1529 (1971); (b) F. R. Jensen and D. D. Davis, *ibid.*, **93**, 4048 (1971).

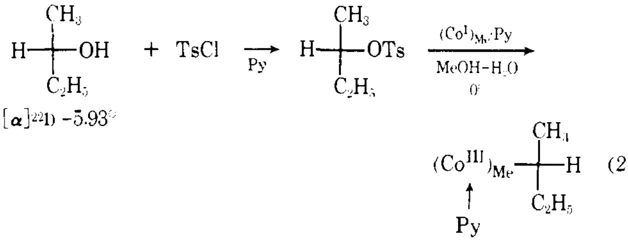
(9) F. R. Jensen, V. Madan, and D. H. Buchanan, *ibid.*, **92**, 1414 (1970).

(10) C. A. Grob and W. Bauman, *Helv. Chim. Acta*, **38**, 594 (1955).

(11) Retention times on a 10-ft QF-1 (firebrick) column at 148°: **2**, 7.8 min; **4**, 10.0 min.

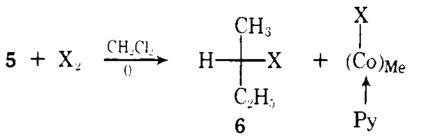
(12) D. D. Davis and F. R. Jensen, *J. Org. Chem.*, **35**, 3410 (1970).

sec-butylcobaloxime[13] (**5**) was too highly colored to give a measurable rotation on several polarimeters.[14] Cleavage of the carbon–cobalt bond by either bromine or iodine at 0° in methylene chloride and isolation of the product by preparative gas chromatography gave *sec*-butyl halides of the same configuration[12] as the starting alcohol (eq 2 and 3). Cleavage by chlorine also occurs with predominant inversion but the exact stereospecificity has not been determined. Previously it has been shown that the alkylation of cobaloxime(I) occurs with inversion at carbon.[9] Therefore, the reaction sequences 2 and 3 demonstrate that the postulated electrophilic cleavages also occur with inversion of configuration at carbon.



(2)

5



(3)

6a, X = Br, yield = 24%,
[α]^{22}D −12.56° (neat); overall retention = 85%
b, X = I, yield = 10%,
[α]^{22}D −13.72° (neat); overall retention = 95%

The observed net loss in stereospecificity in reactions 2 and 3 likely occurs in part in reaction 2. Thus, when **5** is allowed to stand for several hours with an excess of cobaloxime(I), reisolated, and subjected to bromodemetalation, 2-bromobutane 70% racemized is obtained.[15] Apparently this racemization occurs by repeated S$_N$2 displacements by cobalt(I) on carbon. The low yields in reactions 1 and 3 result, at least in part, from competing reactions of bromine with the dimethylglyoxime ligand.

The carbon–cobalt bond in alkylcobalamins and alkylcobaloximes is very hindered to front-side attack. The discovery of the facile electrophilic cleavage by bromine with inversion on carbon leads to the expectation that even bulky electrophiles might bring about such cleavages with highly hindered organometallic compounds.

Also, these results provide another example of the electrophilic inversion pathway which is favored when: (a) the organometallic compound is unable to coordinate with the incoming group; (b) the leaving metal is not an exceedingly strong Lewis acid.[8b]

Considerable current interest exists regarding the possible electrophilic cleavage of methyl B$_{12}$ by mercuric ion in lake and river bottoms to produce "methylmercury." All cleavages of carbon–metal bonds by mercuric ions whose stereochemistry is known proceed by retention of configuration. In certain systems it has been established that mercury has an apparent small steric requirement (*e.g.*, the bromomercuri group has no conformational preference in cyclohexanes)[16] and therefore front-side attack cannot be eliminated. Schrauzer and coworkers[3] have postulated without supporting evidence that the mercuric ion cleavage of carbon–cobalt bonds occurs with inversion of configuration on carbon. No stereochemical evidence is available, and their relative rate data for cleavage of various alkyl derivatives are not in accord with the relative rate profile expected for an S$_E$2 inversion process.[8b]

Acknowledgment. Support of this research by the National Institutes of Health under Grant No. GM 15373 and a Postdoctoral Fellowship to D. H. B. is gratefully acknowledged.

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[13] Elemental analyses and infrared and nmr spectra are all in accord with the proposed structure of this compound.

[14] No rotation was observed on solutions sufficiently dilute to allow passage of light on Zeiss (photoelectric) or Bendix-143A (Faraday effect) polarimeters or by ORD or CD measurements on a Cary-60 instrument. However, "ghost" rotations were observed on the Zeiss instrument, under conditions where the samples were essentially opaque to light.

[15] Unpublished results with V. Madan.

[16] F. R. Jensen and L. H. Gale, *J. Amer. Chem. Soc.*, **81**, 6337 (1959).

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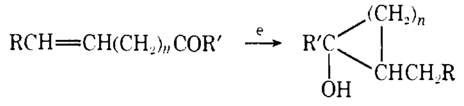
Electroorganic Chemistry. VIII. Intramolecular Cycloaddition of Nonconjugate Olefinic Ketones to Form Cyclic Tertiary Alcohols

Sir:

Attempts to synthesize cyclic tertiary alcohols (**1**) by the intramolecular reactions of organometallic reagents formed from halo ketones are generally unsuccessful due to the extreme difficulty of the generation of such organometallics.[1] In the present study, we wish to describe a novel electrochemical method of synthesis of **1** through the intramolecular cyclization of nonconjugated olefinic ketones, initiated by the electron transfer from an electrode to the carbonyl group. The stereochemistry of the alcohols **1** obtained by the electrochemical method differs from that of those prepared by treatment of cyclic ketones with the Grignard reagent. The electroreduction of 6-hepten-2-one (**2**) (0.03 mol) in the mixed solvent of dioxane (50 ml) and methanol (10 ml) containing tetraethylammonium *p*-toluenesulfonate (20 g) as the supporting electrolyte was carried out at the cathode potential of −2.7 V *vs.* sce (0.2 A) using carbon rod electrodes. The cathodic and anodic chambers were separated by a ceramic cylinder. After about 3 F/mol of electricity was passed, 1,2-dimethylcyclopentanol (**3**) was obtained in 66% yield.



1

3 was identified by comparison of its ir and nmr spectra and its gas chromatographic behavior with those of the independently prepared sample.[2] The exclusive

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[1] E. J. Corey and I. Kuwajima, *J. Amer. Chem. Soc.*, **92**, 395 (1970).