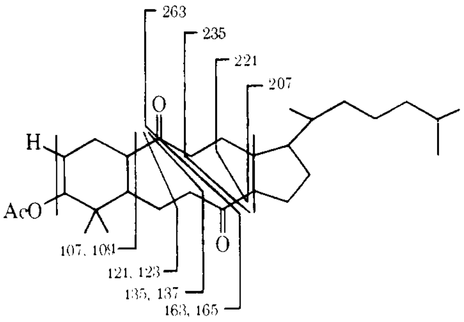
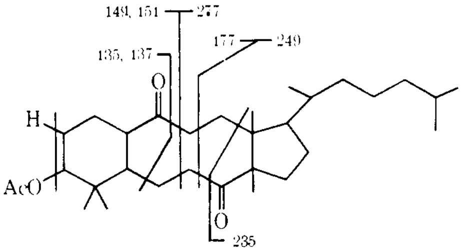
m/e 456, and closely resembles that of LH_2-Ac, but with corresponding peaks 14 mass units lower.

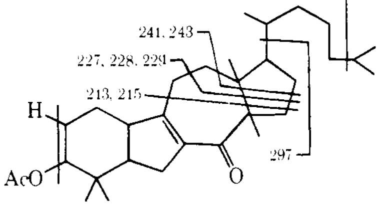
To establish the presence of the 10-H and the $\Delta^{(8,9)}$ double bond, AH_2-Ac was oxidized with RuO_4 to the secodiketone AH_2O_2-Ac (VIII), a product analogous to those similarly[1a] secured from LH_2-Ac and 18-nor-LH_2-Ac. A high resolution mass spectrum (70 eV) of AH_2O_2-Ac revealed the parent ion at *m/e* 488.3865 ($C_{31}H_{52}O_4$) with a base peak at *m/e* 95. The major fragmentations are shown in VIIIa and VIIIb. Transannular condensation of VIII to the desmethyl abeo triterpenoid IX (R_c = 4.31) occurred in concentrated HCl-HOAc or during glc. Mass spectral fragmentations indicative of structures IXa and IXb confirm the assignment II to the original norsterol A.



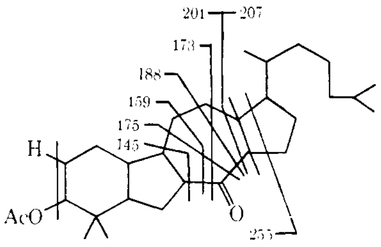
VIIIa



VIIIb



IXa



IXb

The mass spectrum of BH_2-TMSE closely resembled that of AH_2-TMSE. The desmethyl abeo compound derived from the RuO_4 oxidation product of BH_2-Ac was identical in mass spectral and glc properties with that obtained from AH_2-Ac. Evidently the A and B structures must differ in their relative configurations at C-10, since in the derived secodiketone an enolizable proton at this site may epimerize during the trans annular condensation to the abeo compound IX.[15] Since nmr data call for an A-B trans juncture in A, we conclude that B is the corresponding A-B cis counterpart III. In corroboration, the pmr properties of *C*-methyls in the A series (*vide supra*) differ markedly from those in B. In keeping with trends previously observed for *cis*-decalins,[16] the chemical shifts in B (A-B cis) fall at distinctly lower fields than those in the A (A-B trans) cases; thus, in B-Ac, nonallylic methyls appear at δ 1.05, 1.11, 1.17, and 1.19.[9,17]

Acknowledgment. The authors are indebted to Dr. J. R. Trudell, Stanford Medical Center, for mass spectral data and interpretations, Dr. M. Bramwell, Dr. Lois Durham, and Mrs. K. S. Rozema-Meyer for nmr determinations, and Mr. K. Hovius for technical assistance. Financial support was provided by the Netherlands government (J. A. S.), National Institutes of Health (GM 10421 to E. E. v. T.), American Heart Association (grant-in-aid), and a USPHS Research Scientist Award (MH 47413) (to R. B. C.).

[15] Assignment of C-10 stereochemistry in the abeo compound IX is not possible on the basis of available information.

[16] J. I. Musher, *J. Amer. Chem. Soc.*, **83**, 1146 (1961).

[17] This work, started at the University of Groningen and completed at Stanford University, is detailed and discussed in the doctoral thesis submitted to the University of Groningen (April 1971) by J. A. S.

* Address correspondence to this author at the Department of Chemistry, Stanford University.

E. E. van Tamelen,* J. A. Smaal
Department of Chemistry, University of Groningen
Groningen, Netherlands
Department of Chemistry, Stanford University
Stanford, California 94305

R. B. Clayton
Department of Psychiatry, Stanford University
Stanford, California 94305

Received April 30, 9171

Importance of σ-Bonding Effects in the Photolysis of *trans*-Difluorobis(ethylenediamine)chromium(III)

Sir:

The controversy concerning the explanation, or even correlation, of the facts thus far determined in studies on the photoaquation of Cr(III) complexes continues to be vibrant.[1-5] At the center of current discussion are the "rules" that Adamson proposed in 1967.[6] The first of these predicts the stoichiometry of the product of photoaquation of Cr(III) complexes by stating that the "axis having the weakest average crystal field will be the one labilized." Implicit in any attempt to rationalize this rule is, in our opinion, the assumption that photoaquation takes place from the lowest lying quartet excited state. In at least one case

---

[1] E. Zinato, R. D. Lindholm, and A. W. Adamson, *J. Amer. Chem. Soc.*, 91, 1076 (1969).

[2] P. Riccieri and H. L. Schläfer, *Inorg. Chem.*, **9**, 727 (1970).

[3] V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970.

[4] M. F. Manfrin, L. Moggi, and V. Balzani, *Inorg. Chem.*, **10**, 207 (1971).

[5] A. D. Kirk, *J. Amer. Chem. Soc.*, 93, 283 (1971).

[6] A. W. Adamson, *J. Phys. Chem.*, 71, 798 (1967).

Table I. Photochemical Yields of $Cr(en)(enH)H_2OF_2^{2+}$, **1**[a]

Time × 10^2, sec	$[Cr(en)(enH)H_2OF_2^{2+}]/I_a$ × 10^{-2}, sec
1.5	0.68 (1)[b]
3.0	1.5 ± 0.6 (2)
4.5	2.6 (1)
6.0	2.3 ± 0.3 (2)
7.5	3.6 (1)
9.0	3.7 ± 0.4 (2)
12.0	4.5 ± 0.6 (2)
18.0	6.2 (1)
28.0	6.7 (1)
34.0	6.5 (1)

[a] Temperature 21°; 0.1 *N* $HClO_4$. [b] The number in parentheses corresponds to the number of determinations.

Table II. Product Quantum Yields[a]

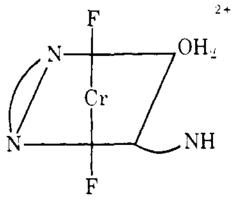
Band	Composition	Eluent	Φ
	F^-	45 ml of 0.15 *M* HCl	≤0.08
1	*trans*-$Cr(en)_2F_2^+$	35 ml of 0.5 *M* HCl	0.63 ± 0.15[b]
2	$Cr(en)(enH)H_2OF_2^{2+}$	50 ml of 0.75 *M* HCl	0.46 ± 0.07
3		20 ml of 1.0 *M* HCl	0.06[c]
4		20 ml of 1.5 *M* HCl	0.05[c]
5		20 ml of 3.0 *M* HCl	0.03[c]

[a] Temperature 21°; 0.10 *M* $HClO_4$. [b] Quantum yield for disappearance of *trans*-$Cr(en)_2F_2^-$. [c] Precision is ±20%.

there has been published some direct experimental support for the concept that reactivity does, or at least can, occur from the lowest lying excited quartet state.[7] If we follow this line of reasoning, then the nature of the lowest lying quartet state will be important in predicting photoreactivity. In Cr(III) complexes of octahedral geometry, this state has the approximate composition $t_{2g}{}^2e_g{}^1$; in the case of complexes of lower symmetry, that orbital of the two of e_g type that is lowest in energy should be important. For several years we have been concerned with the population of an orbital of this type—a σ-antibonding orbital—by reduction of metal ion complexes.[8,9] In this note we test the validity of a σ-bonding model in predicting the axes of labilization in photoaquations of Cr(III) complexes in which the lowest lying σ-antibonding orbital is populated by electronic excitation.

There have been a number of spectroscopic analyses of *trans*-$Cr(en)_2F_2^+$;[10-12] the polarization experiments of Dubicki, Hitchman, and Day[11] have firmly established that at the ground-state internuclear separation a molecular orbital with considerable $d_{x^2-y^2}$ character is the lower of the two lowest lying σ-antibonding orbitals.[13] If this ordering is maintained in the distorted geometry of the excited states, then population of the lowest lying quartet state by irradiation in the $^4B_{1g} \rightarrow {}^4E_g$ transition should involve population of a state with considerable antibonding character in the *xy* plane. Carrying through with this analysis, we would anticipate that large bond distortions occur in the *xy* plane and that consequently an ethylenediamine would be labilized in the photoaquation process rather than a fluoride. We confirm this prediction below. *trans*-$[Cr(en)_2F_2]ClO_4$ was prepared by a minor modification[14] of a literature procedure.[15] Cr, N, and F analyses agree with the calculated ones; the complex exhibits extinction coefficients in agreement with some in the literature:[15] λ, Å (ε, M^{-1} cm^{-1}) 5250 (16.3), 4660 (21.1), 4000 (12.8), 3500 (14.5). Photolysis was carried out using a 500-W xenon lamp as a source; the light was passed through shutters and filters (Oriel G-522-5200 interference filter) to give a band centered at 5200 Å with a band width of about 100 Å. Actinometry was performed using *trans*-$Cr(NH_3)_2(SCN)_4^-$ as described by Wegner and Adamson.[16] Samples, typically 30 ml of 0.015 *M* *trans*-$Cr(en)_2F_2^+$ in 0.10 *M* $HClO_4$, were photolyzed in a 10-cm spectrophotometer cell thermostated at 21° in a water-filled cell holder and stirred by means of a small magnetic stirring bar. Photolysis times ranged from 2.5 to 55 min.

Separation of the photolyzed solution by ion-exchange chromatography revealed four products, one of which predominates. The spectral [λ 5190 Å (ε 40 M^{-1} cm^{-1}), 3660 (18.6)] and ion-exchange characteristics of this major product are identical with those of $Cr(en)(enH)(H_2O)F_2^{2+}$, a compound previously found as the thermal aquation product of *trans*-$Cr(en)_2F_2^+$.[14] This complex contains a monodentate ethylenediamine ligand; the structure was inferred to be **1**. The quantum yield for the production of **1** was



1

determined from the function

$$[Cr(en)(enH)(H_2O)F_2^{2+}]/I_a = \phi t$$

where I_a is the number of einsteins absorbed per unit volume in a given time interval *t;* this ranged from 2.3 to 2.9 × 10^{-6} einstein sec^{-1} $l.^{-1}$. The concentration of **1** was corrected for thermal aquation during photolysis. A plot of $[Cr(en)(enH)(H_2O)F_2^{2+}]/I_a$ was linear for photolysis times up to 15 min, but curved thereafter due to inner-filter effects.[17] The quantum yield was

---

(7) S. N. Chen and G. B. Porter, *Chem. Phys. Lett.*, **6**, 41 (1970); see also G. B. Porter, S. N. Chen, H. L. Schläfer, and H. Gausmann, *Theor. Chim. Acta*, **20**, 81 (1971).

(8) C. Bifano and R. G. Linck, *J. Amer. Chem. Soc.*, **89**, 3945 (1967).

(9) R. G. Linck, *Inorg. Chem.*, **9**, 2529 (1970), and references therein.

(10) L. Dubicki and R. L. Martin, *Aust. J. Chem.*, **22**, 839 (1969).

(11) L. Dubicki, M. A. Hitchman, and P. Day, *Inorg. Chem.*, **9**, 188 (1970).

(12) D. A. Rowley, *ibid.*, **10**, 397 (1971).

(13) The F–Cr–F axis is taken as the *z* axis.

(14) S. C. Pyke and R. G. Linck, *Inorg. Chem.*, in press.

(15) J. Glerup, J. Josephsen, K. Michelsen, E. Pedersen, and C. E. Schäffer, *Acta Chem. Scand.*, **24**, 247 (1970).

(16) E. E. Wegner and A. W. Adamson, *J. Amer. Chem. Soc.*, **88**, 394 (1966).

(17) The photoproducts absorb more strongly than does *trans*-Cr-

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.

Acknowledgment. This work was supported by a Research Grant from the Academic Senate of the University of California, San Diego. We are grateful for that support.

$(en)_2F_2^+$. 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).

Stephen C. Pyke, R. G. Linck*
Chemistry Department, Revelle College
University of California, San Diego, La Jolla, California 92037

Received May 27, 1971

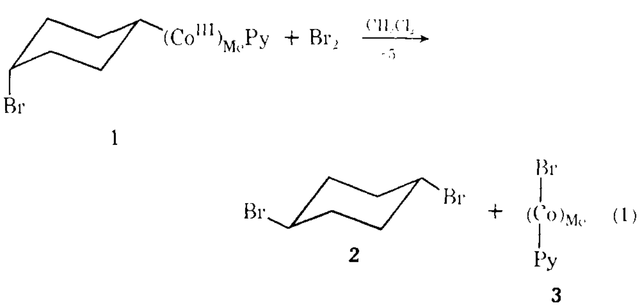
Halogen Cleavage of Carbon–Cobalt Bonds. Demonstration of Inversion at Carbon[1]

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

---

(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).