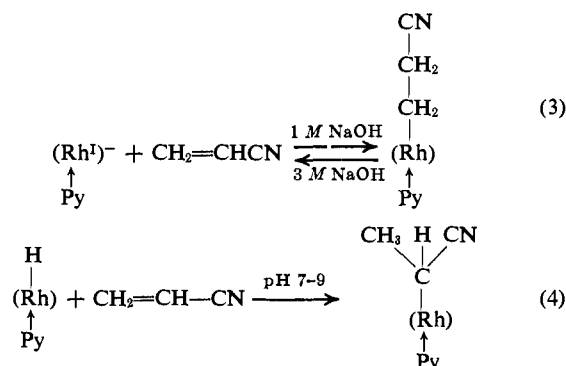


the near identity of the electronic environment of the methyl group in both compounds. *Anal.* Calcd for  $C_9H_{19}N_4O_5Rh$ : C, 29.51; H, 5.23; N, 15.30. Found: C, 29.47; H, 5.35; N, 15.15. In the optical spectrum of methylaquorhodoxime the band at lowest energy is observed at  $403\text{ m}\mu$  ( $\epsilon\ 4.8 \cdot 10^3$ ). The corresponding transition in the cobaloxime occurs at  $448\text{ m}\mu$  ( $\epsilon\ 1.53 \cdot 10^3$ ) and has been assigned to a metal-carbon CT transition. Methylaquorhodoxime is less sensitive to light than methylaquocobaloxime, yielding mainly methane as the termination product of the methyl radical formed on photolysis. The reaction of the methylaquorhodium compound with pyridine yields methylpyridinerhodoxime, mp  $\sim 162^\circ$  dec. *Anal.* Calcd for  $C_{14}H_{24}N_5O_4Rh$ : C, 39.35; H, 5.20; N, 16.39. Found: C, 39.50; H, 5.31; N, 16.15. Ethylpyridinerhodoxime, mp  $\sim 171^\circ$  dec, prepared similarly, produces ethylene on photolysis and thermal decomposition. *Anal.* Calcd for  $C_{15}H_{24}N_5O_4Rh$ : C, 40.82; H, 5.48; N, 15.87. Found: C, 40.78; H, 5.65; N, 15.67. The Rh(I) nucleophile reacts with acrylonitrile in 1 M NaOH to produce  $\beta$ -cyanoethylrhodoxime. The compound undergoes slow elimination back into acrylonitrile and rhodoxime(I) in 3 M aqueous NaOH (eq 3) and thus is more alkali resistant than the corresponding cobaloxime.<sup>8</sup> The rhodium hydride reacts with acrylo-



nitrile exclusively to produce the  $\alpha$ -cyanoethyl derivative (eq 4), as has been noted in the cobaloxime system<sup>8</sup> and in reactions of acrylonitrile with Lewis-base adducts of hydridorhodium(III) chloride.<sup>9</sup> Both isomers have been characterized by analysis and their ir and nmr spectra. *Anal.* Calcd for  $C_{16}H_{23}N_6O_4Rh$ : C, 41.21; H, 4.97; N, 18.02. Found ( $\beta$  isomer): C, 41.25; H, 5.02; N, 18.16, mp  $\sim 170^\circ$  dec. Found ( $\alpha$  isomer): C, 41.22; H, 5.03; N, 18.12, mp  $\sim 221^\circ$  dec. The striking analogy between cobaloximes and rhodoximes becomes obvious from the determination of the Pearson nucleophilicity<sup>10</sup> of  $(\text{Rh}^I)^-$  under conditions identical with those employed for  $(\text{Co}^I)^-$ .<sup>11</sup> The average nucleophilicity of  $13.7 \pm 0.4$  is smaller than that of the cobaloxime(I) (14.3 for  $\text{OH}^-$  as the axial base). The  $\text{S}_{\text{N}}2$  reactions of  $(\text{Rh}^I)^-$  are slower compared to those of  $(\text{Co}^I)^-$  presumably because of the greater size of the  $4d_{z^2}$  orbital or  $4d_{z^2}-5p_z$  hybrid compared to the analogous orbitals of cobalt. The relative rate profiles of Rh(I) and Co(I) reactions are very similar, however (Figure 1). The "iridoxime(I)" nucleophile, in con-

(8) G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, **89**, 1999 (1967).

(9) K. C. Dewhirst, *Inorg. Chem.*, **5**, 319 (1966).

(10) R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, **90**, 319 (1968).

(11) G. N. Schrauzer and E. Deutsch, *ibid.*, **91**, 3341 (1969).

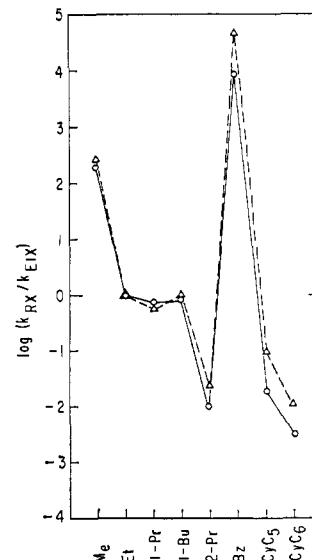


Figure 1. Rate profiles for  $\text{S}_{\text{N}}2$  reactions of rhodoxime(I) (axial base  $\text{OH}^-$ ) ( $\circ-\circ$ ) and of cobaloxime(I) (axial base tributylphosphine) ( $\Delta-\Delta$ ) at  $25^\circ$ , 0.1 *F* in methanol.

trast, is difficult to generate analogously due to the substitution inertness of, e.g.,  $\text{ClIr}(\text{Dmg})_2\text{HCl}$ .<sup>12</sup> Ethylpyridineiridoxime, accordingly, is produced only in trace amounts by reductive alkylation. The compound (dec pt  $\sim 250^\circ$ ) is obtained in better yield by the Grignard procedure. The dark brown complex produces a 2:1 mixture of ethylene and ethane on pyrolysis. Organorhodoximes thus are surprisingly similar to cobaloximes except for a greater stability of the metal-carbon bonds. This suggests that corrins containing rhodium instead of cobalt could be interesting vitamin  $\text{B}_{12}$  inhibitors with little if any biological activity of their own. This prediction is supported by the established weak inhibiting effect of methylaquorhodoxime upon the corrin-dependent evolution of methane by cell extracts of *Methanobacillus omelianskii*,<sup>13,14</sup> where methylaquocobaloxime has been shown<sup>15</sup> to be a substrate almost as efficient as methylcobalamin.

(12) W. W. Lebedinski and L. A. Fedorow, *Izv. Akad. Nauk, Sekt. Platina*, **15**, 29 (1938); cf. "Gmelins Handbuch der anorganischen Chemie," Vol. 67, Verlag Chemie, Berlin, 1939, p 181.

(13) M. P. Bryant, B. C. McBride, and R. S. Wolfe, *J. Bacteriol.*, **95**, 1118 (1968).

(14) We thank Dr. J. M. Wood, University of Illinois, Urbana, for testing the enzymatic activity of methylaquorhodoxime.

(15) B. C. McBride, J. M. Wood, J. W. Sibert, and G. N. Schrauzer, *J. Amer. Chem. Soc.*, **90**, 5276 (1968).

(16) Visiting Scholar, UCSD 1969-1970, from the Department of Chemistry, The University of New Hampshire, Durham, N. H.

(17) This work was supported by Grant GP 12324 of the National Science Foundation.

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### Selection Rules for Mass Spectrometry. An Example of a Photochemical Analogy

Sir:

We present the first complete study of a system designed to test selection rules for electrocyclic reactions induced by electron impact.

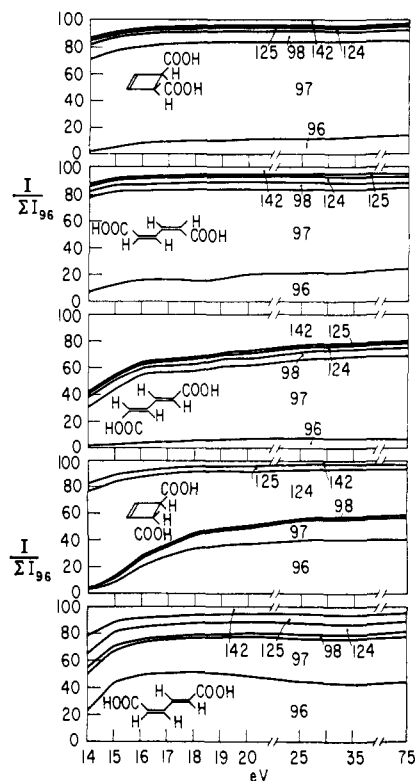


Figure 1. Intensity variation with ionizing energy for isomers.

The stereochemistry of the ring opening of *cis*- and *trans*-3,4-cyclobut-1-enedicarboxylic acid (CCBDA and TCBDA, respectively) and other cyclobutene derivatives to form isomers of the butadiene system, and that of examples of the reverse reaction, have been studied under thermolytic and photolytic conditions,<sup>1</sup> and shown to conform to the accessibility of structures predicted by the Woodward-Hoffmann rules.<sup>2</sup>

The mass spectra of *cis,cis*-muconic acid (CCMA), *cis,trans*-muconic acid (CTMA), *trans,trans*-muconic acid (TTMA), CCBDA, and TCBDA were obtained at high and low voltages.<sup>3</sup> The peak intensity data from the upper end of the spectra for these compounds are illustrated in Figure 1 in an additive clastrogram.<sup>4</sup> The ions of *m/e* 96, 97, 98, 124, 125, and 142 carry >85% of the total ion current at all ionizing voltages investigated. These peaks are also the only ones which show prominent differences in the spectra of the five compounds.

(1) (a) R. Criegee, *Angew. Chem. Intern. Ed. Engl.*, **7**, 559 (1968), and references cited therein; (b) W. G. Dauben in "Reactivity of the Photoexcited Organic Molecule. Proceedings of the 13th Conference on Chemistry, University of Brussels, October, 1965," Interscience Publishers, New York, N. Y., 1967, p 171; (c) (a butadiene photochemistry) R. Srinivasan, *J. Amer. Chem. Soc.*, **90**, 4498 (1968); (d) (cyclobutene thermal isomerization) R. E. K. Winter, *Tetrahedron Lett.*, 1207 (1965); (e) (CCBDA, TCBDA thermal isomerization) E. Vogel, *Angew. Chem.*, **66**, 640 (1954); R. E. K. Winter, unpublished work.

(2) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965); R. Hoffmann and R. B. Woodward, *Accounts. Chem. Res.*, **1**, 17 (1968).

(3) Because of the thermal instability of several of these compounds, the spectra were obtained with the direct-probe inlet. The melting points afterward were the same as before, so isomerization did not occur.

(4) These clastrograms, which we adopt for clarity, differ from those devised by Kiser<sup>5</sup> in that they additively show the fraction of ion current carried by the major ions at each voltage studied; each ion intensity is plotted as a band above the bands for ions of lower *m/e*. The bandwidth is proportional to the observed current produced by that particular ion.

(5) R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 191.

The spectral data for CCBDA are most similar to those of CCMA and also resemble those of TTMA.<sup>6</sup> The Woodward-Hoffmann rules would establish accessibility between these three compounds by a disrotatory process through an excited electronic state,<sup>7</sup> as would the PMO approach,<sup>8</sup> and it appears that ionization caused by electron impact produces similar populations of ions in the three cases, thereby establishing a formal similarity to their photochemical behavior.

Except for the loss of water from TCBDA, its spectrum is fairly similar to that of CTMA; this correspondence is not entirely satisfactory. However, very weak metastable peaks were observed for several processes (Table I), and these again support similarity

Table I. Observed Metastable Peaks in the Spectra of Diacid Isomers<sup>a</sup>

Transition	CCBDA	CCMA	TTMA	TCBDA	CTMA
1 142 → 124 (108.3)		X	X	X	X
2 142 → 97 (66.3)	X	X	X		
3 142 → 96 (64.9)					
4 124 → 97 (75.8)					
5 124 → 96 (74.3)	X		X	X	X
6 97 → 69 (49.1)	X	X	X		
7 97 → 68 (48.2)				X	X

<sup>a</sup> X = weak metastable observed. The patterns for metastables 2, 6, and 7 are significant.

between CCMA, TTMA, and CCBDA on the one hand and CTMA and TCBDA on the other. The CCMA, TTMA, and CCBDA compounds all show metastables of the same approximate intensity (within a factor of 3)<sup>10</sup> for the loss of CO from the *m/e* 97 ion ( $[49.1]/[97] \approx 4 \times 10^{-4}$ ), while in the spectra of TCBDA and CTMA no metastable for this process was observed. Further, the *m/e* 96 ion from TCBDA and CTMA shows an extremely small metastable for the loss of CO ( $[48.2]/[96] \approx 6 \times 10^{-5}$ , the limit of detectability of our instrument).

These results form only one example. It is unsafe to generalize on the similarity of mass spectral decompositions, ring openings, and rearrangements to reactions of excited species in solution. The existence of correlations of intensities of ions with Hammett  $\sigma$  constants<sup>11</sup> indicates that at least for a few systems, mass spectral fragmentation takes place with only vibrational excitation; the stereochemistry of cyclopropyl ring

(6) The only major difference is the intensity of  $M^+$  in TTMA; this compound also seems to have a lower IP than the other compounds.

(7) See ref 2: "... electrocyclic transformations within odd-electron systems should follow the same stereochemical course as the even-electron system containing one further electron..." The decomposition characteristics (*vide infra*) put the reactions into class II.<sup>8</sup>

(8) R. C. Dougherty, *J. Amer. Chem. Soc.*, **90**, 5780 (1968). Application of the PMO method to this system indicates that the transition state is antiaromatic.<sup>9</sup>

(9) Cf. M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1969, p 326.

(10) The magnitude of the factor is partly a result of difficulty in measuring these very small peaks.

(11) M. M. Bursley and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 529 (1966).

opening at high voltage is a further example unless there is prior thermal rearrangement.<sup>12</sup> On the other hand, low-lying excited states in aromatic systems can govern their reactivity.<sup>13</sup> While symmetry and simple MO arguments support our results, more complete calculations of the energetics are desirable.<sup>14</sup> We plan these as well as empirical studies of systems containing only  $\pi$  electrons, to parallel established sigmatropic rearrangements and electrocyclic reactions of solution chemistry.

(12) M. S. Baird and C. B. Reese, *Tetrahedron Lett.*, 2117 (1969).

(13) R. A. W. Johnstone and S. D. Ward, *J. Chem. Soc., C*, 1805, 2540 (1968); but see M. J. Bishop and I. Fleming, *ibid.*, 1712 (1969).

(14) Cf. D. T. Clark and R. A. Armstrong, *Theor. Chim. Acta*, **14**, 370 (1969).

(15) Research Fellow of the Alfred P. Sloan Foundation, 1969–1971.

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### Nucleophilic Reactions of Fluoroolefins. Evidence for a Carbanion Intermediate in Vinyl and Allyl Displacement Reactions

Sir:

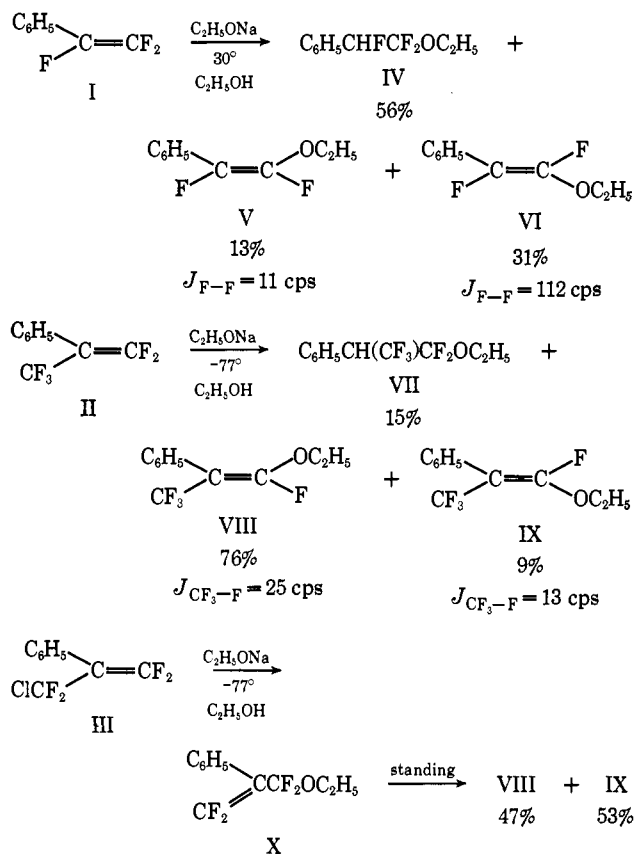
The reactions of nucleophiles,  $N^-$ , with fluorinated olefins can lead to three types of products. In the presence of a proton-donating solvent, SH, the addition of NH across the double bond can occur, while in the absence of a readily available proton either vinyl or allyl displacement of halide may take place. However, the preferential displacement of chloride occurs rather than the addition of NH even in good protic solvents such as alcohols. Qualitatively, these reactions have been well documented in the literature.<sup>1</sup> We felt that these fluorinated olefins could therefore provide a good system for a quantitative study of nucleophilicities. First, a detailed mechanistic investigation was initiated and we wish to report some interesting aspects of these studies.

Three olefins,  $\alpha,\beta$ -trifluorostyrene (I), 2-phenylperfluoropropene (II), and 3-chloro-2-phenylperfluoropropene (III), were chosen to react with sodium ethoxide in absolute ethanol. Addition products were expected from I and II and allylic displacement of chloride was expected from III. The allylic ether, X, was obtained from III. However, I yielded 44% of the vinyl ethers, V + VI, and II gave 85% of the vinyl ethers, VIII + IX. The product ratios of VI/V = 2.5 and VIII/IX = 8.3 indicated that there was some stereoselectivity in the formation of these vinyl ethers. There was no trace of X formed from the reaction of II. The purified allylic ether X rearranged on standing to give an almost 1:1 ratio of VIII:IX.<sup>2</sup> Structural assignments were

(1) An excellent review of this area was made by R. D. Chambers and R. H. Mobbs, *Advan. Fluorine Chem.*, **4**, Chapter 3 (1965).

(2) A similar rearrangement of  $CH_3OCF_2CF=CF_2$  has been reported by B. L. Dyatkin, L. S. German, and I. L. Knunyants, *Dokl. Akad. Nauk SSSR*, **114**, 320 (1957).

made on the basis of fluorine-19 nmr spectra and the coupling constants for the various *cis-trans* isomers agreed well with those reported in the literature.<sup>3</sup> Unsaturated ethers arising from the displacement of fluoride are not uncommon products from cyclic fluoroolefins,<sup>4</sup> but are definitely not the expected product from acyclic fluoroolefins.<sup>1</sup> The possibility of VIII and IX arising from the saturated ether VII was ruled out since the dehydrofluorination reaction was at least six orders of magnitude slower than the reaction of ethoxide with II.<sup>5</sup>



There is little argument that addition and vinylic displacement reactions proceed through a carbanion intermediate; however, differences of opinion usually arise in discussing whether or not allylic displacement reactions go through an intermediate carbanion<sup>4</sup> or go through a concerted  $\text{SN}2'$  mechanism<sup>6</sup> similar to those postulated in hydrocarbon systems. One operational check for the presence of an intermediate carbanion would be a kinetic study. Bunnett has made use of the "element effect" as a criterion to differentiate between a one-step  $\text{SN}2$ -like mechanism and the two-step mechanism involving a metastable intermediate in activated aromatic nucleophilic substitution reactions.<sup>7</sup> If the displacement of two different halogens like fluoride and chloride occurs at a similar rate, then the breaking of the carbon-halogen bond cannot be in-

(3) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, Chapter 11.

(4) J. D. Park, J. R. Lacher, and J. R. Dick, *J. Org. Chem.*, **31**, 1116 (1966).

(5) H. F. Koch and A. G. Toczko, unpublished results.

(6) W. T. Miller, J. H. Fried, and H. Goldwhite, *J. Amer. Chem. Soc.*, **82**, 3091 (1960).

(7) J. F. Bunnett, E. W. Garbisch, Jr., and K. M. Pruitt, *ibid.*, **79**, 385 (1957).