

ion reactions of *exo*-2-bicyclo[2.2.2]octen-5-yl derivatives (VI); (ii) the "Goering" series (G), VIII, IX, Xc, previously obtained<sup>5</sup> from *endo*-2-bicyclo[2.2.2]octen-5-yl derivatives (X); (iii) a miscellaneous group including product XI,<sup>6</sup> apparently derived by hydride shift, product XIIb, derived by protonation-deprotonation, and product IId or IIIId, derived without rearrangement. The latter material is the single most abundant product in the acetolyses. Preliminary results indicate that the pattern of product selectivity (L vs. G) in aqueous acetic acid deamination (where the rearranged products are largely alcohols), or in aqueous acetolysis, is not substantially different from that observed in glacial acetic acid. It is significant that very little *endo*- or *exo*-2-bicyclo[2.2.2]octenyl products (VI or X) are formed in any of the reactions, even under conditions where they would have survived.<sup>7</sup>

The rearranged portion from the deamination and from both acetolyses with *syn* starting materials (II) contains more G- than L-products, the preference being about 2.5 to 1 in deamination and somewhat higher in acetolysis. Starting materials of *anti* configuration (III) give predominantly L-products of rearrangement; the selectivity in deamination is about 40 to 1, substantially higher than in the *syn* series. The distributions of rearranged products thus cannot be accounted for with the common intermediate I.

One conceivable way of preserving the genetic memory is by stereospecific rearrangement and ion-pair return (IIa or IIb to Xa or Xb, and IIIa or IIIb to VIa or VIb), followed by solvolysis. This route cannot be ruled out for the ROBs and RONs acetolyses, but seems unlikely as the sole mechanism for the nitrosative deaminations, where the role of the counterion presumably would have to be played by molecular nitrogen.

The possibility that the ring expansion is fully concerted with the second step of the rearrangement in each case is remote, since the geometry of both starting systems seems completely unsuited for this. A "partially" concerted mechanism, in which the C-1-C-6  $\sigma$ -electrons of II or the C-2-C-3  $\pi$ -electrons of III interact with C-7 after C-4 has started its migration to the CH<sub>2</sub> side chain, is conceptually distinguishable only in degree from the simplest formulation, which involves the deformationally isomeric ions Ia and Ib. These readily accommodate the observed specificity:

(5) H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1992 (1961); H. L. Goering, R. W. Greiner, and M. F. Sloan, *ibid.*, **83**, 1391 (1961); H. L. Goering and D. L. Towns, *ibid.*, **85**, 2295 (1963). We thank Professor Goering and Mr. R. Anderson for supplying detailed procedures for the preparation of VIII and IX before publication.

(6) Identified by vapor chromatographic comparison as such and as the alcohol with authentic samples: cf. R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963), to whom we are indebted for a preprint of their paper. The possibility that our product may be the presently unknown epimer of XI cannot yet be ruled out.

(7) (a) Unidentified peaks in the acetate region of the vapor chromatograms account for about 0.5-3.5% of the total area. Another 2-5% of materials of short retention time (probably hydrocarbons) are present. Substantial amounts of other substances, probably diacetates, also are observed in the acetolyses of *anti*-ROBs (IIIa) and *anti*-RONS (IIIb). (b) From *syn*-amine IIc in acetic acid, the L-series, IV, V, VIc, VII, is formed in the approximate relative proportions 56:1:3:0; the G-series, VIII, IX, Xc, is distributed as 43:1:1. From *anti*-amine IIIc, the L-series is 187:5:11:1; of the G-products, only VIII is found (in an amount about equal to V), while IX and Xc are present in undetectably small amounts. These distributions are to be compared with those obtained from VIa<sup>4a</sup> (L-series, 30:0:1.5:1) and Xa<sup>9</sup> (G-series, 247:1.25:1).

the axis (dotted line) of the empty p-orbital of Ia lies nearly parallel to the C-1-C-7 bond, delocalization of which traps the cation in the Goering system. The geometry of Ib is correspondingly favorable for interaction between C-2 and the C-5-C-6  $\pi$ -electrons, which generates the Le Bel system. To judge by the specificities,  $\pi$ -trapping in the Ib  $\rightarrow$  L-system is more efficient than  $\sigma$ -trapping in the Ia  $\rightarrow$  G-system.

Although some drift *within* each series occurs under acetolytic conditions, interconversion of G- to L-series products or *vice versa* is very slow there or under deamination conditions. The crossover observed in acetolysis occurs to at most a minor extent *via* the nortricycylcarbiny compounds XIIa or XIIb, since these do not give substantial quantities of G- or L-products under the reaction conditions. Thus, the most likely path for crossover is the single twitch by which Ia or Ib can relax to I.<sup>8</sup>

(8) The full paper will consider such subtle questions as whether Ia and Ib represent potential energy minima; whether there is explicative benefit in considering the species as having delocalized three-center bonding involving C-2, C-3, and C-4; and whether the differences in behavior of the II and III systems are attributable to transitory differences in the local environment of cation I rather than to two structurally different cations.

(9) Dow Chemical Company Fellow, 1964-1965.

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## Reactions of Olefins with Xenon Fluorides<sup>1,2</sup>

Sir:

Direct addition of fluorine to olefins is usually difficult to control and is often accompanied by substitution or cleavage of the carbon chain or both.<sup>3</sup> The discovery of the xenon fluorides<sup>4</sup> made available a series of fluorinating agents which appeared particularly attractive for controllable selective fluorinations. Along with our current interests in the chemistry of xenon compounds, we wish to report the reactions of olefins with xenon fluorides.

The three fluorides, XeF<sub>2</sub>, XeF<sub>4</sub>, and XeF<sub>6</sub>, are known to be progressively more reactive as the amount of fluorine in the molecule increases.<sup>5</sup> They form elemental xenon as the only product which is easily separated from the organic products. Reactions may be carried out in the vapor phase at room temperature, and the problems associated with the use of solvents are thus eliminated.

The apparatus used in these investigations is very similar to that used for the preparation of the xenon fluorides,<sup>4</sup> being made mainly from nickel or monel.

(1) Work at the University of Chicago was supported by a grant from the U. S. Atomic Energy Commission.

(2) Based on work performed in part at the Argonne National Laboratory under the auspices of the U. S. Atomic Energy Commission.

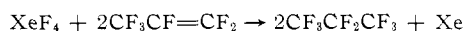
(3) For example see M. Hudlicky, "Chemistry of Organic Fluorine Compounds," Pergamon Press, New York, N. Y., 1961, p. 68.

(4) (a) H. H. Claassen, H. Selig, and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962); (b) J. L. Weeks, C. L. Chernick, and M. S. Matheson, *ibid.*, **84**, 4612 (1962); (c) J. G. Malm, I. Sheft, and C. L. Chernick, *ibid.*, **85**, 110 (1963); (d) see also review for the preparation in "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill. 1963, Chapter 2.

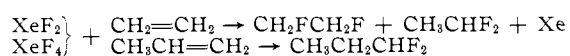
(5) N. Bartlett, *Endeavour*, **23**, 3 (1964).

Purified reactants were condensed at  $-195^\circ$  into a 130-ml. nickel vessel. The vessel was allowed to warm to room temperature and the course of the reaction was followed by observing the change in pressure. It was assumed that the reaction had reached completion when no further pressure change was noted. The reaction products were separated at the vacuum line by trapping at different temperature and by gas chromatography. They were identified by their infrared, n.m.r., and/or mass spectra.

In a typical experiment a mixture of  $\text{XeF}_4$  (0.75 mmole) and perfluoropropene (1.28 mmoles) was allowed to react in a nickel vessel at room temperature. The products were removed from unreacted  $\text{XeF}_4$  *in vacuo* at  $-78^\circ$  and trapped at  $-195^\circ$ . They were shown to be perfluoropropane and xenon in stoichiometric amounts. Perfluoropropane was identified by comparison with an authentic sample. We observed that  $\text{XeF}_6$  is considerably more reactive than  $\text{XeF}_4$  while  $\text{XeF}_2$  is less reactive. Under similar conditions,  $\text{XeF}_6$  reacts with perfluoropropane to give both  $\text{C}_2\text{F}_6$  and  $\text{CF}_4$  as the major products, indicating extensive cleavage, while  $\text{XeF}_2$  is unreactive even after six days.



An interesting rearrangement occurs when xenon fluorides react with aliphatic olefins. At room temperature, ethylene reacts with  $\text{XeF}_2$  or  $\text{XeF}_4$  to give 1,1- and 1,2-difluoroethane in 35 and 45% yields, respectively, together with a minor component which is not yet identified. However the reaction of propylene with  $\text{XeF}_2$  or  $\text{XeF}_4$  gives 1,1-difluoropropane as the main product (*ca.* 65% yield). Allylic fluorination may have occurred also to a certain extent as hydrogen fluoride was detected in the reaction mixture.



The relative instability of secondary fluorides<sup>6</sup> and the increasing stability of compounds with fluorine atoms attached on the same carbon<sup>7</sup> suggest a possible pathway for formation of the *gem*-difluorides; the *vic*-difluorides, presumably the initial products of the reactions, isomerize under the reaction conditions to give the *gem*-difluorides. We detected a slow isomerization of 1,2-difluoroethane to 1,1-difluoroethane in  $\text{CCl}_4$  solution upon standing at room temperature, which is in agreement with the suggested pathway.

The reactions studied so far indicate the potential of the xenon fluorides as fluorinating agents in organic chemistry. The mechanism of the reactions and further studies extending the work to acetylenic and aromatic systems are in progress.

(6) For example, see A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, p. 12.

(7) J. Hine, *J. Am. Chem. Soc.*, **85**, 3239 (1963).

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## Charge-Transfer Interaction in Organic Polymers<sup>1</sup>

Sir:

The charge-transfer interaction between electron donors and acceptors has been a subject of both theoretical and experimental interest.<sup>2</sup> Certain types of charge-transfer complexes of simple organic compounds exhibit semiconducting properties,<sup>3</sup> and charge-transfer interaction has been suggested as an intermediate stage in biological reactions.<sup>4</sup> The present communication deals with the intramolecular interaction of electron-donating and electron-accepting groups in organic polymers.

One major difficulty in the preparation of organic polymers containing both electron-donating and electron-accepting functional groups is that organic monomers containing strong electron-accepting groups, *e.g.*, trinitrostyrene (TNS, I), are excellent inhibitors to both ionic and free-radical polymerizations.<sup>5</sup> Apparently, the reactive intermediates in the polymerizations, ions or radicals, are rendered inactive by interaction with the electron-accepting groups. Several attempts made to prepare polymers and copolymers of TNS have been unsuccessful.<sup>6</sup>

Although TNS could not be polymerized in previous attempts, it might be copolymerized with monomers containing electron-donating groups. The electron-donating group may interact with the strong electron-accepting trinitrophenyl function, thus freeing the vinyl group for polymerization. The copolymerization of TNS with nitrogen-containing vinyl monomers was thus attempted with the nonbonding electrons of the nitrogen atom acting as the electron donor. The copolymerization of TNS and 4-vinylpyridine (4-VP, II) occurred exothermically upon mixing at room temperature. After the mixture was dissolved in pyridine and treated with ether, copolymers of molecular weight ranging from 6000 to 8000 were obtained in about 60% yield. The presence or absence of oxygen made no difference. Apparently sufficient delocalization occurred during the charge-transfer process to initiate the polymerization.<sup>7</sup> The relative proportion of the two monomers in the copolymers could be varied by adjusting the mole ratio of the two monomers in the polymerization mixture, *e.g.*, a 1:1 mixture of the monomers reacted to give a 1:2 (TNS-4-VP) copolymer while a 2:1 (TNS-4-VP) mixture gave a 1:1 copolymer. The copolymers formed were somewhat soluble in chloroform, acetone, or dimethylformamide but were insoluble in ether or aliphatic

(1) The work is supported in part by the U. S. Atomic Energy Commission, Contract No. AT(11-1)-1043, and by the Alfred P. Sloan Foundation.

(2) For a review on the interaction of electron donors and acceptors, see R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962). For applications of charge-transfer complexes, see L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1963, pp. 122-125.

(3) D. S. Acker, *et al.*, *J. Am. Chem. Soc.*, **82**, 6508 (1960), and later papers; M. M. Labes, R. Sehr, and M. Bose, *J. Chem. Phys.*, **33**, 868 (1960).

(4) For discussions on the charge-transfer interactions in biological systems, see A. Szent-Gyorgyi, "Introduction to a Submolecular Biology," Academic Press Inc., New York, 1960, p. 76; E. Kosower, "Molecular Biochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 180.

(5) R. H. Wiley and L. C. Behr, *J. Am. Chem. Soc.*, **72**, 1822 (1950).

(6) The molecular weights were determined with a Mechrolab vapor phase osmometer.

(7) Polymerizations initiated by charge-transfer interactions have been reported by H. Scott, G. A. Miller, and M. M. Labes, *Tetrahedron Letters*, 1073 (1963).