Fluoroazirines. Synthesis and Polymerization

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Hexafluoropropene and triethylammonium azide react with loss of nitrogen to form 2,3-difluoro-2-trifluoro-methyl-2H-azirine in 25% yield. This azirine can be isomerized with hydrogen fluoride to 2,2-difluoro-3-tri-fluoromethyl-2H-azirine. Both azirines polymerize an-ionically with extreme ease to polyaziridines. Warm-ing of these polymers causes a unique exothermic bond migration in which the aziridine rings are opened and azomethine links introduced.

Fluoroalkyl and fluoroalkenyl azides have apparently received no study beyond that reported by Knunyants and Bykhovskaya.[1] These workers prepared 2-H-perfluoroalkyl azides by attack of azide ion on hexa-fluoropropene and on octafluoroisobutene in the presence of a proton source. Their finding that satu-rated azide I is stable toward aqueous base and to normal conditions of purification and storage was confirmed in this study. On the other hand, vinyl azide II, ob-tained from azide ion and hexafluoropropene, was found to decompose with loss of nitrogen at room temperature. Fluorocarbanions like III have been proposed as discrete intermediates in such reactions of fluoroolefins with anions.[1-3]

$$CF_3CF=CF_2 \; + \; N_3^- \; \longrightarrow \; [CF_3CFCF_2N_3]$$

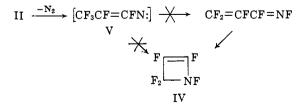$$CF_3CHFCF_2N_3 \qquad\qquad CF_3CF=CFN_3 \; + \; F^-$$
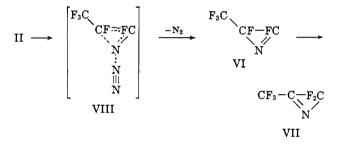$$I \qquad\qquad\qquad\qquad II$$

Evidence that the decomposition of unsaturated azide II leads to the unusual azetene IV was also re-ported by Knunyants and Bykhovskaya.[1] A reaction to form IV could conceivably proceed by migration of fluorine from carbon to nitrogen, but the stability of C–F bonds and relative instability of N–F bonds make such a rearrangement less likely than other reaction paths. Azetene IV could also arise by direct insertion of nitrene V into a C–F bond, but the tightly held valence shell electrons of covalently bound fluorine

are quite insensitive to electrophilic attack. This unprecedented reaction was therefore investigated further.

Reaction of hexafluoropropene with triethylam-monium azide in *sym*-tetrachloroethane at −5° was carried out as described previously.[1] The resulting solution of pentafluoropropenyl azide (II), analyzed by infrared spectroscopy, decomposed at a convenient rate at 25–40°. The major product, evolved as a gas, b.p. −17°, was shown by analytical and spectral data to be 2,3-difluoro-2-trifluoromethyl-2H-azirine (VI). Variable amounts of the isomeric fluoroazirine VII were also isolated as a by-product.

Our attempts to detect IV as a product from decom-position of the unsaturated azide II were unsuccessful. Comparison of the physical and spectral data for fluoroazirines VI and VII with those reported for IV shows marked differences. We are unable to ration-alize the spectral data reported in ref. 1.

Formation of azirine VI may go *via* nitrene V in a manner akin to that of the unfluorinated α-azido-styrene.[4] Participation by the double bond with more or less concerted formation of the three-membered ring and loss of nitrogen is indicated by the ease with which vinyl azide II is decomposed thermally as com-pared to saturated fluoroazide I. Therefore, we assume that the free nitrene is not an intermediate, but rather that a gradual decline to azirine VI occurs from a low-lying transition state resembling VII. A related type of assisted decomposition of unconjugated alkenyl azides has recently been shown to occur in sterically favored cases.[5] A triazole intermediate in the de-composition of II is improbable, since even fluorinated tetrazoles are stable at 100°.[6]
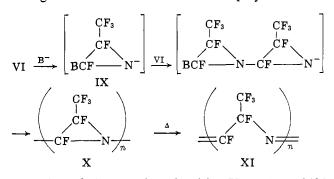
Azirine VI can be stored at 25° in dry, acid-washed glassware, but tends to polymerize in contact with metal containers and is exceptionally sensitive to basic reagents. Bases probably attack the ring at the 3-position to form an aziridine anion IX, which can eliminate fluoride ion and undergo further degradation

(1) I. L. Knunyants and E. G. Bykhovskaya, *Proc. Acad. Sci. USSR Chem. Sect.* (English Transl.), **131**, 411 (1960).

(2) C. G. Krespan, *J. Org. Chem.*, **27**, 1813 (1962), and references therein.

(3) S. Ándreades, *J. Am. Chem. Soc.*, **86**, 2003 (1964), demonstrated the formation of fluorocarbanions as long-lived intermediates from monohydrofluorocarbons plus base.

(4) (a) G. Smolinsky, *ibid.*, **83**, 4483 (1961); (b) *J. Org. Chem.*, **27**, 3557 (1962).

(5) A. L. Logothetis, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, Abstracts of Papers, pp. 65, 66S.
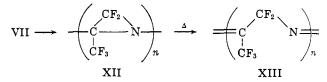
(6) W. G. Finnegan, R. A. Henry, and R. Lofquist, *J. Am. Chem. Soc.*, **80**, 3908 (1958).

reactions. Under conditions conducive to anionic polymerization, *i.e.*, catalytic amount of base, low temperature, and high concentration of azirine, a colorless transparent elastomer can be obtained in essentially quantitative conversion. The n.m.r. and infrared spectra show that the original structure is retained, but that the double bond is saturated, confirming the unusual structure X for this polymer.
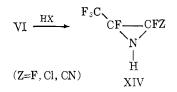

Heating of elastomeric polyazirine X at about 140° causes a sudden exothermic reaction which occurs with virtually no evolution of volatiles and results in a very viscous oil. Spectral data clearly support the occurrence of bond migration along the polymer chain to form polyazomethine XI. This rapid rearrangement consists of a concerted electron shift and involves no migration of groups or atoms. Differential thermal analysis revealed the expected exotherm from 92 to 188° with a maximum at 147°.

2,2-Difluoro-3-trifluoromethyl-2H-azirine (VII), frequently obtained in low yield, is believed to arise from rearrangement of the major product VI. Catalytic isomerization (VI → VII) has been demonstrated with hydrogen fluoride, a probable impurity in the crude samples of VI since even water reacts readily with VI to liberate hydrogen fluoride. The new azirine VII, isolated by v.p.c., is also sensitive to bases and undergoes anionic polymerization with extreme ease to form polyaziridine XII. Thus, solid opaque homopolymer XII is formed readily at −78° with tetraethylammonium cyanide catalyst. Although isomer VI polymerized in the crystalline phase at −196° under electron bombardment, the new azirine VII was essentially unaffected under these conditions.

Structure XII is proposed without direct evidence from n.m.r., since this polymer is difficultly soluble in all solvents tried and, moreover, undergoes a vigorous exothermic rearrangement at only 40°. The viscous polymer obtained from this reaction corresponds only partially to polyazomethine XIII, since spectral evidence indicated the presence of a considerable proportion of structure XI.

Evidence that the isomerization of fluoroazirine VI to VII proceeds by an addition–elimination mechanism is provided by the formation of an adduct of azirine VI with an equivalent of hydrogen fluoride. This adduct is believed to be 2,2,3-trifluoro-3-trifluoromethylaziridine (XIV, Z = F), a derivative which can theo-

retically dissociate in two ways to give an equilibrium mixture containing hydrogen fluoride and both azirines.[7] The conversion of one azirine to another by a small amount of hydrogen fluoride fits the assumption that these equilibria are attained. Isolation of azirine VII as the thermodynamically favored product might be expected in view of the fluoroalkyl rather than the fluoro substituent on the double bond.

The azirines (VI and VII) and their polymers (X, XI, XII, and XIII) all react with H_2O, the monomers being very sensitive to hydrolysis.

An infrared absorption band characteristic of all the three-membered fluorinated nitrogen heterocycles prepared in this study occurs at 6.7–7.0 μ. This band may prove to be useful in diagnosing small-ring fluorinated heterocycles, since tetrafluorothiirane[8] has also been found to absorb at 6.95 μ in the infrared while neither hexafluorocyclopropane[9] nor 1,2-bis(trifluoromethyl)-3,3-difluorocyclopropene[10] absorbs in this region. The C–F stretching absorptions fall at wave lengths somewhat greater than 7 μ, and hence do not interfere. However, C–H absorptions do fall in this region, precluding a comparison with the spectra of small-ring hydrocarbon analogs.

Experimental[11]

2,3-Difluoro-2-trifluoromethyl-2H-azirine (VI) *and 2,2-Difluoro-3-trifluoromethyl-2H-azirine* (VII). An anhydrous ethereal solution of hydrazoic acid was prepared.[12] Addition of this solution (about 600 ml.) to a solution of 50.0 g. (0.50 mole) of triethylamine in 500 ml. of anhydrous ether was carried out with cooling until the mixture became distinctly acidic. Solvent and excess hydrazoic acid were removed from the voluminous precipitate of triethylammonium azide by evacuation (no external source of heat) until essentially constant weight was attained. The solid azide does volatilize slowly at 25°, but ether was nevertheless removed as completely as possible at this stage to avoid subsequent, untimely polymerization of the azirines. *The triethylammonium azide so obtained (a hygroscopic salt presumed to be toxic and potentially explosive) was never manipulated.*[13] Dry *sym*-tetrachloroethane, 400 ml., was drawn into the evacuated and ice-cooled

(7) J. A. Young, S. N. Tsoukalas, and R. D. Dresdner, *J. Am. Chem. Soc.*, **80**, 3604 (1958), report the dissociation of $(CF_3)_2NH$ into HF and $CF_3N=CF_2$ at elevated temperatures.

(8) Unpublished result from these laboratories.

(9) R. N. Hazeldine, *J. Chem. Soc.*, 3764 (1953).

(10) W. Mahler, private communication.

(11) F^{19} n.m.r. spectra were obtained at 56.4 Mc. on a Varian Associates high-resolution spectrometer and are reported relative to the low-field peak resonance of 1,1,2-trichloro-1,2,2-trifluoroethane as internal reference.

(12) L. F. Audrieth and C. F. Gibbs, *Inorg. Syn.*, **1**, 78 (1939).

(13) A. Cirulis and M. Straymanis, *J. prakt. Chem.*, **161**, 65, (1942), report the only previous preparation of triethylammonium azide. They obtained a liquid product, presumably due to absorbed water, which could not be crystallized. Reference 6 records the use of similar alkylammonium azides easily prepared *in situ* from sodium azide, the appropriate chlorides, and polar solvents like dimethylformamide. However, we found such solvents unsuitable for preparation of the sensitive fluorinated vinyl azide and fluoroazirines.

flask containing the azide, bringing about rapid solution of the salt. Using this procedure, no difficulties were experienced.

The freshly prepared solution of triethylammonium azide in tetrachloroethane was immediately cooled at $-5°$ and stirred vigorously while 75 g. (0.50 mole) of hexafluoropropene was passed in through a sintered glass stick over a period of 1.5–2 hr. The hexafluoropropene reacted as it was added until near the end of the reaction. The cold reaction mixture was extracted with 200 ml. of ice-cold dilute hydrochloric acid, then with 200 ml. of ice-cold water, and dried over anhydrous magnesium sulfate at 0°. *Caution: hydrazoic acid may be liberated during the acid wash. Testing with aqueous ferric chloride provides a convenient indication of inorganic azides.* Volatiles were removed from the stirred reaction mixture at 0° (50–10 mm.) for 3 hr. and collected in a trap cooled with liquid nitrogen. The volatiles obtained from four such runs were combined, dried at 0° over anhydrous magnesium sulfate, and filtered at 0° to give a solution of pentafluoropropenyl azide (II) along with the saturated azide I in tetrachloroethane. A sample withdrawn from the vapor phase of this solution had important infrared bands at 4.6, 5.7, 7.3, 8.2, and 8.6 μ which are assigned to II.

This solution was allowed to warm to 25° in a flask connected in series through a vertical, water-cooled reflux condenser to a $-80°$ trap, a drying tube, and a wet-test meter. Volatile material collected in the $-80°$ cold trap during evolution of the first 3 l. of nitrogen was discarded since it contained nearly all the unreacted hexafluoropropene and little azirine. Removal of hexafluoropropene at this stage prevented difficulties in purification of the fluoroazirines later on. The impure azirines were collected during evolution of the remainder of the nitrogen (15 l.). Distillation of this product in an acid-washed, low-temperature still gave 45 ml. (74 g., 25% yield) of 2,3-difluoro-2-trifluoromethyl-2H-azirine (VI), b.p. $-17°$, contaminated with <5% of 2,2-difluoro-3-trifluoromethyl-2H-azirine (VII) and 2H-heptafluoropropane.

The pot liquid remaining after N_2 evolution gave on distillation 30 ml. (43 g., 25%) of 2H-hexafluoropropyl azide (I), b.p. 51° (lit.[1] b.p. 51°), identified by n.m.r. and infrared spectroscopy.

Further purification of the azirines was accomplished by gas chromatography at -20 to $0°$ on a firebrick column coated with the ethyl ester of "Kel-F" acid No. 8114. Under these conditions, isomer VII eluted first, VI second, and 2H-heptafluoropropane last. The azirines were routinely stored in acid-washed glass vessels at $-78°$ without rearrangement or polymerization. Highly purified samples were stable as liquids at 25° in sealed glass vessels (see Table I).

Anal. (*azirine VI*). Calcd. for C_3F_5N: F, 65.50; mol. wt., 145. Found: F, 65.70; mol. wt., 143 (gas density), 145 (mass spectrum).

Important infrared bands occurred in the gas phase at 5.43, 6.76, 7.45, 8.23, 8.88, and 9.88 μ. The F^{19} n.m.r. spectrum contained a doublet centered at +695 c.p.s. ($J = 50$ c.p.s.), a doublet centered at +1755 c.p.s. ($J = 50$ c.p.s.), and a broad doublet centered at +4685 c.p.s. ($J = 52$ c.p.s.) in the ratio 3:1:1. Each half of the broad doublet is resolvable to a quadruplet at low temperature.

Table I. Mass Spectra of Azirines VI and VII

m/e	Fragment	VI, %	VII, %
12	C	5.5	7.4
31	CF	58.2	108
50	CF_2	36.6	28.2
69	CF_3	100	100
76	C_2F_2N	48.9	77
95	C_2F_3N	10.7	29.9
100	C_2F_4	9.6	31.6
119	C_2F_5	55.3	...
126	C_3F_4N	22.7	45.7
145	C_3F_5N	44.8	8.7

Anal. (*azirine VII*). Calcd.: mol. wt., 145. Found: mol. wt., 145 (mass spectrum).

Important infrared bands occurred in the gas phase at 5.70, 5.80, 6.95, 7.86, 8.21, and 9.66 μ. The F^{19} n.m.r. spectrum contained a singlet at +245 c.p.s. and another at +2255 c.p.s. in a 3:2 ratio.

Polyaziridine X. A glass trap containing 6.6 g. (4.0 ml.) of 2,3-difluoro-3-trifluoromethyl-2H-azirine (VI) was cooled to $-78°$ and 0.16 g. of pyridine was added. Slow polymerization occurred. The mixture was warmed slowly over a 2-hr. period to $-15°$ and held there for 1 additional hr. Evaporation of volatiles left an almost quantitative yield of colorless, transparent elastomer. This polymer, soluble in CF_2-$ClCFCl_2$, was found to have an inherent viscosity at 25° of 0.17 at 0.2% concentration. Principal infrared absorption of a film cast from $CF_2ClCFCl_2$ occurred at 6.92 μ with broad bands in the 7.5–10-μ region. The 5.44-μ band in the monomer assigned to C=N was missing; a minor amount of unsaturation was indicated by a weak band at 5.70 μ. Major resonances occurred in the F^{19} n.m.r. spectrum at +450, +3395, and +5990 c.p.s. in the ratio 3:1:1. A very small band was also observed at +770 c.p.s.

Anal. Calcd. for $(C_3F_5N)_x$: C, 24.84; F, 65.50; N, 9.66. Found: C, 25.26; F, 63.57; N, 9.60.

Polyazomethine XI. Two grams of polymer X above was dissolved in 30 ml. of $CF_2ClCFCl_2$, sealed in a platinum tube, and heated at 175° for 10 min. under 33 atm. Essentially complete conversion to a thick, pale yellow grease occurred. Some loss in molecular weight was indicated by an inherent viscosity of 0.08 for a 0.2% solution in $CF_2ClCFCl_2$ at 25°. The infrared spectrum now contained a strong band for unsaturation at 5.70 μ, and bands in the 7.5–10-μ region for C–F, but none in the region of 6–7.5 μ. The F^{19} n.m.r. spectrum contained bands at -2612, +746, and +4242 c.p.s. in the ratio 1:3:1.

Virtually no rearrangement was induced by heating X in $CF_2ClCFCl_2$ at 75° for 10 min., and after 10 min. at 150° rearrangement was only about 90% complete. The bulk polymer, without moderating solvent, underwent exothermic, rapid, and complete rearrangement when heated to 140°.

Crude Polyaziridine XII and Polyazomethine XIII. A flask containing 1.6 g. (1.0 ml.) of 2,2-difluoro-3-trifluoromethyl-2H-azirine (VII), 4 ml. of HCF_2CF_2-CH_2Cl, and 10 mg. of tetraethylammonium cyanide at $-196°$ was warmed to $-78°$. The reaction mixture rapidly gelled. The mixture was warmed to 25° over a 1-hr. period, diluted with chloroform, and filtered. The insoluble white powdery polymer was

obtained in nearly quantitative conversion. The infrared spectrum of this powder had a strong band at 6.9 as well as absorption at 7.5–10 μ. Weak absorption also occurred at 5.8 μ.

A suspension of 0.3 g. of the above polymer in 15 ml. of $CFCl_2CF_2Cl$ was heated in a platinum tube at 80° for 10 min. Evaporation of solvent left a thick, colorless grease. Infrared absorption of a film occurred at 5.7–5.8 μ and in the 7.5–10-μ region. No absorption was found at 6.0–7.5 μ. The F^{19} n.m.r. spectrum showed at least nine types of fluorine, including those similar to polymer XI. Rearrangement of the bulk polyaziridine XII occurred vigorously and completely, commencing at only 40°.

HX Adducts of 2,2,3-Trifluoro-3-trifluoromethylaziridine. Equimolar amounts of hydrogen fluoride and 2,3-difluoro-2-trifluoromethyl-2H-azirine (VI) were added manometrically, 0.5 atm. of each, to a 300-ml. stainless steel cylinder at 25°. After having stood for 1 day, the contents gave an infrared spectrum containing new intense bands at 3.00 (N–H) and 6.73 μ (hetero-

cycle), while bands characteristic of VI had disappeared; this was taken as evidence for XIV, Z = F. A small amount of isomeric azirine VII was also present.

Similar addition of hydrogen chloride to VI in place of hydrogen fluoride occurred slowly at 25° in the gas phase. After 20 hr. almost all of the starting azirine was gone, and infrared bands assignable to adduct XIV (Z = Cl) at 2.94 and 6.99 μ had appeared. No isomerization to azirine VII was apparent. Similar addition of hydrogen cyanide to VI occurred in 20 hr.; infrared bands assignable to adduct XIV (Z = CN) were found at 2.94 and 6.69 μ, while absorptions due to starting material were nearly absent. As frequently happens, no C≡N band was detected.

Isomerization of Azirine VI to VII. A mixture of 1.8 g. of VI and 10 mg. of anhydrous HF was heated at 50° for 4 hr. at 33 atm. in a sealed platinum tube. There was obtained an almost quantitative conversion of VI to VII, identified by infrared. Lower conversions and polymerization frequently occurred in other experiments, due to the sensitivity of the azirines.

The Synthesis and Study of Pseudo-Aromatic Compounds. V. The Synthesis of 3,4-Benzoheptafulvene, 1,2-Benzoheptafulvene, and 8-Phenyl-1,2-benzoheptafulvene[1]

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Contribution from the Department of Chemistry, The University of California, Santa Barbara, California. Received December 28, 1964

The synthesis of 3,4-benzoheptafulvene, 1,2-benzoheptafulvene, and 8-phenyl-1,2-benzoheptafulvene are described. Analysis of their n.m.r. and infrared spectra indicates that dipolar resonance interactions are of minor importance in the ground state.

Although simple MO calculations indicate that heptafulvene should be an aromatic molecule possessing a substantial π-electron delocalization energy, more advanced calculations indicate that heptafulvene should approximate a polyolefin.[2] The synthesis of heptafulvene and derivatives substituted at the 8-position of heptafulvene has provided data which demonstrates that simple heptafulvenes do not possess characteristics associated with an aromatic system exhibiting pronounced π-electron delocalization.[3–6] However, the

reactivity of heptafulvene has precluded the determination of pertinent data necessary to describe the actual π-electronic interactions within the molecule. The extreme reactivity of heptafulvene can be accounted for by assuming that it is a polyolefin in the ground state and that electrophilic attack leads to an aromatic tropenium ion intermediate.[8]

Fusion of a benzene ring to the heptafulvene ring system should both stabilize the benzoheptafulvenes and increase the polyolefinic character.[7] The relatively lower stability of the benzotropenium ion[8] with respect to the tropenium ion should lessen the tendency for the benzoheptafulvenes to undergo electrophilic attack. M.O. calculations have been done for 3,4-benzoheptafulvene[2] and 1,2-benzoheptafulvene[9] and predict charge delocalization from the ring onto the 8-position and substantial π-electron delocalization energies for both compounds. However, these same calculations also predict a pronounced alternate double- and single-bond character in the seven-membered ring. The syntheses of 2H-benz[*c,d*]azulene and a tetra-

(1) Presented before the Organic Division, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 4–9, 1965.

(2) G. Berthier and B. Pullman, *Trans. Faraday Soc.*, 45, 848 (1949); E. D. Bergmann, E. Fischer, D. Ginsberg, Y. Hrishberg, D. Lauie, M. Mayot, A. Pullman, and B. Pullman, *Bull. soc. chim. France*, 18, 684 (1951); A. Julg, *J. chim. phys.*, 52, 50 (1953); 59, 257 (1962); T. Nakajima and S. Katagiri, *Bull. Chem. Soc. Jaapn*, 25, 910 (1962).

(3) W. Von E. Doering and D. W. Wiley, *Tetrahedron*, 11, 183 (1960).

(4) R. B. Turner, W. R. Meador, W. Von E. Doering, L. H. Knox, J. R. Mayer, and D. W. Wiley, *J. Am. Chem. Soc.*, 79, 4127 (1957).

(5) H. J. Dauben, Jr., and R. B. Medz, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963, Abstracts, p. 75.

(6) D. J. Bertelli, C. Golino, and D. L. Dreyer, *J. Am. Chem. Soc.*, 86, 3329 (1964).

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(9) A. Streitwieser, Jr., private communication.