as a colorless oil, b.p. 72–73° (10 mm.), $n^{25}D$ 1.4068. The fluorine n.m.r. spectrum contained a pair of quadruplets. The proton n.m.r. spectrum showed an AB pattern at 5.13 and 5.87 (J = c.p.s.) of area 1 and a multiplet from 3.50–4.43 p.p.m. of area 2.

Anal. Calcd. for $C_7H_6F_6O_2S$: C, 31.35; H, 2.26; F, 42.51; S, 11.96. Found: C, 30.92; H, 2.28; F, 42.40; S, 12.08.

Dihydropyran–HFTA Adduct.—HFTA, 36.4 g. (0.2 mole), was added dropwise to a stirred solution of 8.4 g. (0.1 mole) of dihydropyran and 10 ml. of methylene chloride cooled to −78°. The reaction mixture was distilled to give 21 g. of HFTA dimer, and 15.5 g. of a pale purple oil, b.p. 57° (4.7 mm.), which solidified upon standing overnight. Recrystallization from pentane gave 10.9 g. of the adduct as colorless prisms, m.p. 36–37°. The fluorine n.m.r. spectrum showed two quadruplets of equal area. The infrared spectrum showed no evidence of unsaturation.

Anal. Calcd. for $C_8H_8F_6OS$: C, 36.09; H, 3.03; F, 42.82; S, 12.04. Found: C, 36.19; H, 3.03; F, 42.89; S, 12.00.

***t*-Butyl Vinyl Sulfide–HFTA Adduct.**—HFTA was added dropwise to a solution of 11.6 g. (0.1 mole) of *t*-butyl vinyl sulfide in 25 ml. of methylene chloride cooled to −78° until a faint blue color persisted. The reaction mixture was distilled to give 33.1 g. of HFTA dimer, b.p. 38° (40 mm.), and 27.7 g. (93%) of 2,2-bis(trifluoromethyl)-4- (or 3-) *t*-butylthiothietane as a colorless liquid, b.p. 38° (0.6 mm.), $n^{25}D$ 1.4252. The infrared, fluorine, and proton n.m.r. spectra appear to be consistent with the assigned structure. The fluorine n.m.r. spectrum showed a typical A_3B_3 pattern.

Anal. Calcd. for $C_9H_{12}F_6S_2$: C, 36.24; H, 4.06; F, 38.22; S, 21.50. Found: C, 36.51; H, 4.14; F, 38.26; S, 22.00.

A portion of this product was oxidized to the monosulfone by the following procedure. Hydrogen peroxide (30%), 10 ml., was added dropwise to a stirred solution of 6.06 g. (0.02 mole) of the thietane and 2 ml. of concentrated hydrochloric acid in 60 ml. of acetic acid at such a rate that the temperature of the reaction mixture remained between 50 and 80°. Water, 100 ml., was then added. The mixture was cooled, and the white precipitate that formed was collected on a filter, washed with water, and recrystallized from alcohol. There was obtained 3.6 g. of the sulfone as colorless prisms, m.p. 166–167°.

Anal. Calcd. for $C_9H_{12}F_6O_2S_2$: C, 32.72; H, 3.67; F, 34.51; S, 19.41. Found: C, 33.12; H, 3.55; F, 34.15; S, 19.55.

Methyl Vinyl Sulfide–HFTA Adduct.—HFTA, 18.2 g. (0.1 mole), was added portionwise to a stirred solution of 3.7 g. (0.05 mole) of methyl vinyl sulfide in 15 ml. of methylene chloride cooled to −78°. The colorless reaction mixture was distilled to give 2.3 g. of adduct, b.p. 40–41° (3.6 mm.), $n^{25}D$ 1.4268. The fluorine n.m.r. spectrum contained two quadruplets of equal area.

Anal. Calcd. for $C_6H_6F_6S_2$: C, 28.12; H, 2.36; S, 25.02. Found: C, 28.21; H, 2.79; S, 25.83.

Fluorimines

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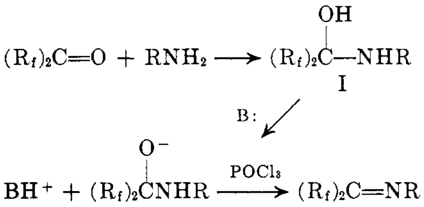
A new one-step procedure for the synthesis of fluorimines [$(R_f)_2C{=}NR$] in high yield is described. Reactions illustrating the predominately electrophilic character of fluorimines are presented along with some new derivatives to indicate their versatility as intermediates.

Reports that α-fluoro ketones can be converted to the usual ketone derivatives with carbonyl reagents are rare.[1] Similarly, attempts to prepare imines from fluoro ketones and amines have been unsuccessful until the present work. Imines of hexafluoroacetone have also been synthesized recently by Knunyants and his coworkers.[2] They used exchange with phosphine imines or an indirect route involving exchange with phenyl isocyanate since they believed the hydroxy amines formed from hexafluoroacetone and amines not to be subject to dehydration.

Amine and ammonia adducts of fluoro ketones are indeed very stable toward loss of water or of amine or ammonia, so that minor amounts of fluoro ketone and fluorimine must be present under equilibrium conditions at ordinary temperatures. Attempts to alter these equilibria by raising the temperature are complicated by a side reaction, similar to the haloform decomposition, in which the geminal hydroxy amine cleaves to fluoroalkane and fluoramide.[3] Chemical dehydration can be induced, however, by taking advantage of the acidity of the hydroxyl group in adduct I[4] to promote reaction at oxygen in basic media.[5]



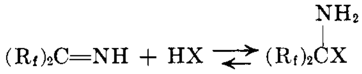
$$(R_f)_2C{=}O + RNH_2 \longrightarrow (R_f)_2\overset{OH}{\overset{|}{C}}{-}NHR \quad \text{I}$$

$$\swarrow \text{B:}$$

$$BH^+ + (R_f)_2\overset{O^-}{\overset{|}{C}}NHR \xrightarrow{POCl_3} (R_f)_2C{=}NR$$

Conversion of a fluoro ketone to an imine, then, can be conveniently accomplished without isolation of the hydroxy amine I by using pyridine as the basic medium, adding the fluoro ketone, then ammonia or the primary amine, and lastly phosphorus oxychloride. Provided that the mixture is cooled to minimize side reactions, yields of 60–80% are easily attained.

The electronegative groups attached to the imine carbon make the double bond electron deficient, so that nucleophiles will attack to form stable adducts. Many of these adducts are without parallel in the chemistry of nonfluorinated amines. *gem* derivatives of type II, where X can be varied considerably, are easily prepared from the corresponding active hydrogen compounds. Adducts with one or more of the fluorimines have been prepared from ammonia, piperazine, hydrazine, methanol, ethylene glycol, cyanic acid,



$$(R_f)_2C{=}NH + HX \rightleftarrows (R_f)_2\overset{NH_2}{\overset{|}{C}}X$$

II

(X = NH_2, $NHNH_2$, NCO, N_3, OCH_3, F, etc.)

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(1) H. E. Simmons and D. W. Wiley [*J. Am. Chem. Soc.*, **82**, 2288 (1960)] noted that, except for hexafluoroacetone semicarbazone, no carbonyl derivatives of fluoro ketones had been claimed.

(2) Y. V. Zeifman, N. P. Gambaryan, and I. L. Knunyants, *Dokl. Akad. Nauk SSSR*, **153**, 1334 (1963).

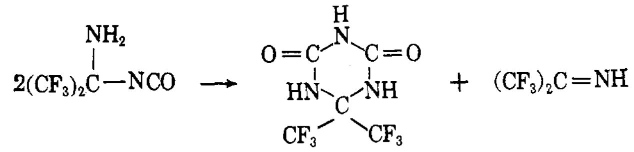
(3) M. Hauptschein and R. A. Braun, *J. Am. Chem. Soc.*, **77**, 4930 (1955).

(4) Properties of various fluoro alcohols, including Brønsted acidity, are discussed by W. J. Middleton and R. V. Lindsey, *ibid.*, **86**, 4948 (1964).

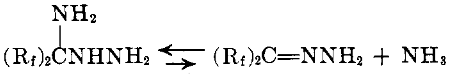
(5) Simmons and Wiley[1] described a similar procedure for alkylating fluoro alcohols.

hydrazoic acid, and hydrogen fluoride. Basic catalysis is generally not necessary, but does enhance reactivity.

The unusual stability of the adducts is illustrated by $(CF_3)_2C(NH_2)_2$, which boils at 91° without decomposition. Because of its negative groups, this *gem*-diamine is virtually neutral and reacts with excess ketene to form only the monoacetyl derivative. Low reactivity of the amine function also allows isolation of the adduct II where X is the free isocyanate group. High inherent reactivity of the isocyanate group was demonstrated by its vigorous reaction with water to form the substituted urea. The amino isocyanate also reacts over an extended period of time with the small equilibrium concentration of free isocyanic acid present in the adduct to give a triazine.



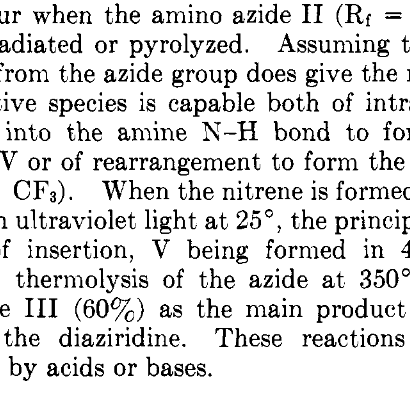
As indicated for the N-phenyl analogs[2] and for the amino isocyanate above, equilibria between imine plus nucleophile and adduct II exist that are displaced greatly toward formation of the adduct. The synthesis of fluoro ketone hydrazones (III) is, in fact, made possible by such an equilibrium, wherein reversal of addition is encouraged by chemically removing the dissociated nucleophile. Thus, the imines may serve as intermediates to carbonyl derivatives not available directly from the fluoro ketones.



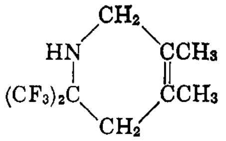
$$(R_f)_2\overset{NH_2}{\overset{|}{C}}NHNH_2 \rightleftarrows (R_f)_2C{=}NNH_2 + NH_3$$

III

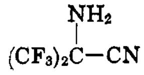
Reactions apparently involving a nitrene intermediate occur when the amino azide II ($R_f = CF_3$, $X = N_3$) is irradiated or pyrolyzed. Assuming that loss of nitrogen from the azide group does give the nitrene IV, this reactive species is capable both of intramolecular insertion into the amine N-H bond to form the diaziridine V or of rearrangement to form the hydrazone III ($R_f = CF_3$). When the nitrene is formed by irradiation with ultraviolet light at 25°, the principal product is that of insertion, V being formed in 43% yield. However, thermolysis of the azide at 350° gives the hydrazone III (60%) as the main product with only 11% of the diaziridine. These reactions were not catalyzed by acids or bases.



Some additions to fluorimines occur with formation of carbon–carbon bonds. Diels–Alder reaction of hexafluoroisopropylidenimine with 2,3-dimethylbutadiene proceeds at 100° to give adduct VI. Base-catalyzed addition of hydrogen cyanide gives the α-aminonitrile[2] VII.



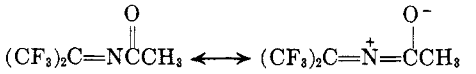
VI



$$\overset{NH_2}{\overset{|}{(CF_3)_2C}}{-}CN$$

VII

Electrophiles like ketene react poorly, if at all, with fluorimines, which are themselves electrophiles. Reaction at the hexafluoroisopropylidenimine N-H bond, however, can be catalyzed by BF_3 to give the acetamide VIII. Fluorinated imines may therefore exhibit amphoteric behavior. The unusual amide bands in the infrared spectrum (5.70 and 5.77 μ) and the singlet F^{19} resonance in the n.m.r. spectrum of VIII indicate substantial dipolar character in the amide group.



$$(CF_3)_2C{=}N\overset{O}{\overset{\|}{C}}CH_3 \longleftrightarrow (CF_3)_2C{=}\overset{+}{N}{=}\overset{O^-}{\overset{|}{C}}CH_3$$

VIII

Since the N-H proton in the imine is acidic, exchange with methyllithium gives the fluorimine lithium salt. Bromination of this salt leads to the light-sensitive N-bromo compound IX, which couples photolytically to the azine X with loss of molecular bromine.

$$(CF_3)_2C{=}NBr \longrightarrow (CF_3)_2C{=}N{-}N{=}C(CF_3)_2$$

IX X

Experimental[6]

Hexafluoroisopropylidenimine.—Pyridine, 500 ml., contained in a 1-l. flask fitted with a condenser cooled with solid carbon dioxide, a mechanical stirrer, thermometer, and a gas inlet tube, was cooled to −25° by means of a solid carbon dioxide–acetone bath. The stirrer was started, and 200 g. (1.2 moles) of hexafluoroacetone[7] was distilled into the flask, keeping the temperature between −25 and −30°. Ammonia, 25 ml. at −78° (*ca.* 20.4 g., 1.2 moles), was then distilled into the stirred reaction mixture, keeping the temperature between −25 and −30°. The cooling bath was replaced with a heating mantle, and the reaction mixture was warmed to 25°. The condenser was replaced with a water-cooled condenser connected to a trap cooled with solid carbon dioxide, and 100 ml. (184 g., 1.2 moles) of phosphorus oxychloride was added dropwise at such a rate that gentle reflux was maintained. The gas that escaped through the condenser was collected in the cold trap. After the addition was completed (*ca.* 30 min.), the reaction mixture was heated to 100° and held there for 30 min. The condensate in the trap was distilled through a 40-cm. packed column to give 138 g. (70% yield) of product as a colorless liquid, b.p. 16–16.5°, m.p. −47°, d^{0}_{4} 1.51, infrared 5.98 μ for C=N. The F^{19} n.m.r. spectrum showed two quartets centered at +5.77 and +7.62 p.p.m. ($J_{FF} = 6$ c.p.s.) of equal area, with the lower field quartet further split to a doublet ($J_{FH} = 2.5$ c.p.s.). The proton n.m.r. spectrum showed a single broad band at 11.8 p.p.m. The ultraviolet spectrum showed λ_{max} 248 mμ (ε 93).

Anal. Calcd. for C_3HF_6N: C, 21.83; H, 0.61; F, 69.07; N, 8.46. Found: C, 21.81; H, 0.76; F, 68.81; N, 8.16.

N-Methylhexafluoroisopropylidenimine.—Hexafluoroacetone, 26 ml. at −78° (0.25 mole), was distilled into a flask containing

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(6) Fluorine n.m.r. spectra were obtained with Varian Associates high-resolution n.m.r. spectrometer operating at 56.4 Mc./sec. Spectra were calibrated in terms of higher field displacement in parts per million (p.p.m.) from the F^{19} resonance of 1,2-difluoro-1,1,2,2-tetrachloroethane used as an external reference. Proton spectra were obtained with a Varian Associates A-60 spectrometer. Spectra were calibrated in terms of lower field displacement in parts per million from the proton resonance of tetamethylsilane used as an internal reference.

(7) Commercial hexafluoroacetone of 99.5+% purity, obtained from E. I. du Pont de Nemours and Co., was used.

125 ml. of pyridine cooled to −25°. Methylamine, 12 ml. at −10° (0.25 mole), was then distilled into the reaction mixture, keeping the temperature between −20 and −30°. The mixture was warmed to 25°, and 25 ml. of phosphorus oxychloride was added dropwise over a period of 30 min. The mixture warmed spontaneously and began to boil. The evolved gases were condensed in a trap cooled by solid carbon dioxide–acetone. The reaction mixture was heated to 90° for 1 hr. The condensate was distilled to give 39.3 g. (87% yield) of product as a colorless liquid, b.p. 34–35°, $n^{25}\text{D}$ <1.3, infrared 5.87 μ for C═N. The F^{19} n.m.r. showed two quartets (J_{FF} = 8 c.p.s.) of equal area centered at −0.33 and +6.12 p.p.m., each split further into quartets (J_{FH} = 2.5 and 1.8 c.p.s., respectively). The proton n.m.r. spectrum showed a multiplet centered at +3.71 p.p.m.

Anal. Calcd. for $C_4H_3F_6N$: F, 63.67; N, 7.83. Found: F, 63.76; N, 7.66.

Chloropentafluoroisopropylidenimine.—A solution of 171 g. (100 ml. at −78°, 0.937 mole) of chloropentafluoroacetone in 500 ml. of pyridine was cooled to −30°, and 20 ml. (about 0.94 mole) of ammonia at −78° was slowly distilled into the mixture. The mixture was then allowed to warm to room temperature and 100 ml. of phosphorus oxychloride was added dropwise over a period of 30 min. An exothermic reaction ensued, and the temperature of the reaction mixture rose to 90° as refluxing began. The lower boiling material was removed from the reaction mixture by distillation, and the fraction that boiled below 100° was redistilled through a spinning-band column. There was obtained 102 g. (60%) of product as a colorless liquid, b.p. 46–47° (mostly 46.7°), $n^{25}\text{D}$ 1.3130. The infrared spectrum contained a band at 5.92 μ for C═N. The F^{19} n.m.r. spectrum showed evidence of two isomeric forms of this imine. The predominant isomer showed a quartet (J_{FF} = 7 c.p.s.) for CF_2 at −4.34 p.p.m. further split to a doublet (J_{FH} = 2 c.p.s.) and a higher field triplet (J_{FF} = 7 c.p.s.) for CF_3 at + 2.83 p.p.m. further split to a doublet (J_{FH} = 2.3 c.p.s.). The lesser isomer showed a quadruplet (J_{FF} = 7 c.p.s.) for CF_2 further split to a doublet (J_{FH} = 1.8 c.p.s.) at −2.08 p.p.m. and a triplet (J_{FF} = 7 c.p.s.) for CF_3 at +5.05 p.p.m. The proton n.m.r. showed a broad singlet centered at +11.6 p.p.m.

Anal. Calcd. for C_3HClF_5N: C, 19.86; H, 0.56; Cl, 19.55; F, 52.34; N, 7.77. Found: C, 20.24; H, 0.75; Cl, 19.64; F, 51.95; N, 7.65.

1,3-Dichlorotetrafluoroisopropylidenimine.—This imine, b.p. 80.5–81.5°, $n^{25}\text{D}$ 1.3608, was prepared in 75% yield by a similar procedure from 1,3-dichlorotetrafluoroacetone and ammonia. The infrared spectrum showed a band at 5.98 μ for C═N. The F^{19} n.m.r. spectrum showed two triplets of equal area centered at −9.04 and −6.91 p.p.m. (J = 9 c.p.s.), and the proton n.m.r. spectrum showed a singlet at +11.54 p.p.m.

Anal. Calcd. for $C_3HCl_2F_4N$: Cl, 35.82; F, 38.38; N, 7.07. Found: Cl, 35.89; F, 38.06; N, 6.90.

1-(Pentafluoroethyl)pentafluoropropylidenimine.[8]—A mixture of 100 ml. of dry pyridine and 75 g. (0.28 mole) of decafluorodiethyl ketone (40 ml. at −78°) was kept below −25° and stirred while 6 ml. of ammonia was added. The mixture was then warmed to room temperature, and 24 ml. of phosphorus oxychloride was added dropwise at a rate sufficient to maintain gentle reflux. Volatile material was distilled into an ice–methanol trap (pot to 100°) and redistilled giving 9.4 g. (13%) of starting ketone and 27.1 g. (42% yield) of the desired imine, b.p. 52°, $n^{25}\text{D}$ 1.3227; infrared showed an N-H band at 3.04 μ and a C═N band at 5.99 μ. The proton n.m.r. exhibited a singlet peak at +12.2 p.p.m., and the F^{19} n.m.r. showed multiplets at +14.9 (area 3), +15.6 (area 3), +48.6 (area 2), and +51.9 (area 2) p.p.m. (internal reference).

Anal. Calcd. for $C_5HF_{10}N$: C, 22.65; H, 0.38; F, 71.41; N, 5.29; mol. wt., 265. Found: C, 23.06; H, 0.64; F, 71.65; N, 5.50; mol. wt., 265 (mass spectrum).

Aminobis(trifluoromethyl)methyl Isocyanate.—Isocyanic acid was added portionwise, about 1 ml. every 30 min., to stirred, refluxing hexafluoroisopropylidenimine (25 ml. measured at −10°, 0.23 mole) until a total of 15 ml. had been added. The mixture was then allowed to stir under reflux overnight. The entire reaction mixture solidified. It was then strongly heated under reduced pressure and the material that distilled was collected in a solid carbon dioxide cooled trap. Redistillation gave 20.8 g. (43%) of product as a colorless liquid, b.p. 86°, $n^{25}\text{D}$ 1.3248. The F^{19} n.m.r. spectrum contained a singlet at +14.9 p.p.m. The infrared spectrum contained a band at 4.4 μ for NCO.

Anal. Calcd. for $C_4H_2F_6N_2O$: C, 23.09; H, 0.97; F, 54.78; N, 13.47. Found: C, 23.56; H, 1.20; F, 55.15; N, 13.50.

One drop of water was added to 0.1 g. of aminobis(trifluoromethyl)methyl isocyanate, and the mixture was shaken vigorously. A reaction ensued, gas was evolved, and the reaction mixture solidified to a white crystalline mass. The solid was dried *in vacuo* over potassium hydroxide to give 0.09 g. of white crystalline solid, m.p. 124–126°. Analysis indicated this solid to be N,N′-bis[aminobis(trifluoromethyl)methyl]urea.

Anal. Calcd. for $C_7H_6F_{12}N_4O$: C, 21.55; H, 1.55; F, 58.43; N, 14.36. Found: C, 22.11; H, 1.69; F, 58.74; N, 15.15.

4,4-Bis(trifluoromethyl)hexahydro-2,6-dioxo-1,3,5-triazine. A 10-g. sample (0.05 mole) of aminobis(trifluoromethyl)methyl isocyanate was examined 10 months after it had been stored in a glass vial, and its was found to be solid. The solid was recrystallized from ethanol to give 5.3 g. (85%) of product as colorless prisms, m.p. 223–225°. The proton n.m.r. spectrum in acetone showed two broad singlets at +9.15 (area 2) and +9.90 p.p.m. (area 1). The infrared spectrum contained bands at 5.74 and 5.83 μ for C═O.

Anal. Calcd. for $C_5H_3F_6N_3O_2$: C, 23.91; H, 1.20; F, 45.40; N, 16.72. Found: C, 24.34; H, 1.36; F, 45.55; N, 16.17.

Hexafluoro-2,2-propanediamine.—Ammonia, 8.5 g. (0.5 mole), was distilled into a flask containing 39 g. (0.24 mole) of hexafluoroisopropylidenimine cooled in an ice bath. After the addition, the mixture was refluxed for 5 min. and then distilled. There was obtained 42.5 g. (97%) of product as a colorless liquid, b.p. 91–91.5°, m.p. 20.5°, $n^{25}\text{D}$ 1.3229. The infrared spectrum contained bands at 2.92 and 3.00 μ for NH_2. The F^{19} n.m.r. spectrum showed a singlet at +15.7 p.p.m. The proton n.m.r. showed a broad singlet at +2.25 p.p.m.

Anal. Calcd. for $C_3H_4F_6N_2$: C, 19.79; H, 2.21; F, 62.61; N, 15.39. Found: C, 20.11; H, 2.28; F, 62.27; N, 15.82.

N-Acetylhexafluoro-2,2-propanediamine.—A stirred mixture of 7.4 g. (0.04 mole) of hexafluoro-2,2-propanediamine and 10 ml. of ketene was refluxed at atmospheric pressure for 1 hr., and then the excess ketene was evaporated. The solid residue was recrystallized from benzene to give 8.0 g. (89%) of product as colorless needles, m.p. 87–88°. A sample was recrystallized from chloroform for analysis. The F^{19} n.m.r. spectrum showed a singlet at +12.14 p.p.m.

Anal. Calcd. for $C_5H_6F_6N_2O$: C, 26.79; H, 2.68; F, 50.87; N, 12.50. Found: C, 27.35; H, 3.15; F, 50.93. N, 12.77.

1,3-Dichloro-1,1,3,3-tetrafluoro-2,2-propanediamine.—Ammonia, 6.6 ml. at −78° (about 0.3 mole), was distilled into a flask containing 39.6 g. (0.2 mole) of 1,3-dichloro-1,1,3,3-tetrafluoroisopropylidenimine. The reaction mixture was refluxed under a Dry Ice cooled condenser for 2 hr. and then distilled. There was obtained 38.3 g. (89%) of product as a colorless oil, b.p. 44.5–45° (10 mm.), $n^{25}\text{D}$ 1.4105. The F^{19} n.m.r. spectrum contained a single peak at −3.80 p.p.m. The proton n.m.r. showed a singlet at +2.25 p.p.m.

Anal. Calcd. for $C_3H_4Cl_2F_4N_2$: C, 16.75; H, 1.88; Cl, 32.98; F, 35.36; N, 13.03. Found: C, 17.01; H, 1.94; Cl, 32.82; F, 35.29; N, 12.37.

N,N′-Bis(2-aminohexafluoroisopropyl)piperazine.—Hexafluoroisopropylidenimine, 11 ml. at −10° (about 0.1 mole), was slowly distilled into a stirred suspension of 4.3 g. (0.05 mole) of piperazine in 50 ml. of ether. The ether was evaporated under reduced pressure, and the white residue was recrystallized from hexane to give 16.9 g. (81%) of product as colorless prisms, m.p. 113–114°. The infrared spectrum contained bands at 2.94, 3.00, and 6.18 μ.

Anal. Calcd. for $C_{10}H_{12}F_{12}N_4$: C, 28.87; H, 2.91; F, 54.78; N, 13.47. Found: C, 29.15; H, 2.91; F, 54.24; N, 13.96.

1,2-Bis(2-aminohexafluoroisopropoxy)ethane.—A mixture of 4.65 g. (0.075 mole) of ethylene glycol, 16 ml. (measured at −10°) of hexafluoroisopropylidenimine (0.15 mole), and 3 drops of triethylamine was stirred at reflux for 24 hr. and then distilled. There was obtained 27.65 g. (94%) of the diamine as a colorless liquid, b.p. 43–44° (0.1 mm.), $n^{25}\text{D}$ 1.3373. The infrared spectrum contained bands at 2.89 and 2.95 μ for NH_2. The F^{19} n.m.r. spectrum contained a singlet at +13.67 p.p.m. The proton n.m.r. spectrum contained a sharp singlet at +3.95 p.p.m. and a broad singlet at +2.40 p.p.m. of equal area.

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(8) We are indebted to Dr. D. M. Gale of these laboratories for this experiment.

Anal. Calcd. for $C_8H_8F_{12}N_2O_2$: C, 24.50; H, 2.06; F, 58.13; N, 7.15. Found: C, 25.00; H, 2.37; F, 58.14; N, 7.54.

2-Methoxyhexafluoroisopropylamine.—Methyl alcohol, 0.75 ml. (0.02 mole), was added to a 2-ml. sample of hexafluoroisopropylidenimine cooled to −10°. The reaction mixture was warmed to room temperature and then distilled to give 1.7 g. of product as a colorless liquid, b.p. 91–92°, n^{25}D 1.3144.

Anal. Calcd. for $C_4H_5F_6NO$: N, 7.11. Found: N, 7.11.

2-Aminohexafluoroisopropylhydrazine.—Hexafluoroisopropylidenimine, 33 g. (20 ml. at −10°, 0.2 mole), was slowly distilled into a flask containing 6.4 g. (0.2 mole) of hydrazine. The reaction mixture was cooled in an ice bath during the addition. Distillation at reduced pressure gave 33.7 g. (85%) of product as a colorless liquid, b.p. 73–74° (45 mm.), n^{25}D 1.3565. The F^{19} n.m.r. showed a singlet at +11.25 p.p.m. and the proton n.m.r. showed three broad singlets at +4.4 (area 1), +3.5 (area 2), and +2.5 p.p.m. (area 2).

Anal. Calcd. for $C_3H_5F_6N_3$: C, 18.31; H, 2.56; F, 57.84; N, 21.32. Found: C, 18.57; H, 2.67; F, 57.68; N, 21.59.

N-Bromohexafluoroisopropylidenimine (IX).—Hexafluoroisopropyldenimine (16 ml. at −10°) (0.15 mole) was slowly distilled into a stirred solution of 87 ml. (0.15 mole) of 5.43% methyllithium in ethyl ether cooled to 0°. The ether was removed by distillation under reduced pressure (Caution: on one occasion when the temperature rose to ~25°, an explosion occurred.), and the residue was redissolved in 75 ml. of benzonitrile. Bromine, 24 g. (0.15 mole), was added dropwise to the stirred solution which was kept below 10°. The reaction mixture was evacuated, and the material that distilled below 40° (2 mm.) was condensed and redistilled. There was obtained 18.7 g. (51%), of IX as a colorless liquid, b.p. 49.5–50°, n^{25}D 1.3346. The infrared spectrum contained a band at a 6.07 μ for C=N. The F^{19} n.m.r. spectrum contained a pair of quartets (J = 7 c.p.s.) centered at +2.07 and +3.01 p.p.m.

Anal. Calcd. for C_3BrF_6N: C, 14.77; Br, 32.75; F, 46.75; N, 5.74. Found: C, 15.46; Br, 31.80; F, 46.55; N, 6.03.

Hexafluoroacetone Azine (X).—N-Bromohexafluoroisopropylidenimine, 3.1 g. (0.013 mole), was sealed in a Pyrex tube and irradiated with a low-pressure mercury arc light for 3 days. The tube was opened, and the lower bromine layer (about 1 g.) was removed. A few drops of 1-octadecene was added to the upper layer to discharge the bromine color, and then the sample was distilled at atmospheric pressure. There was obtained 2.0 g. (94%) of X as a colorless liquid, b.p. 67–67.5°. The F^{19} n.m.r. spectrum contained two broad peaks at −0.11 and +3.90 p.p.m. The infrared spectrum contained a band at 6.00 μ.

Anal. Calcd. for $C_6F_{12}N_2$: N, 13.09. Found: N, 12.79.

N-Acetylhexafluoroisopropylidenimine (VIII).—Hexafluoroisopropylidenimine, 10 ml. at −10° (0.094 mole), contained in a flask, was cooled by an ice–methanol bath. Boron trifluoride was passed into the flask until the reaction mixture was filled with a suspended white solid. Ketene, 10 ml., was then distilled into the reaction mixture with cooling. Distillation of the reaction mixture gave 8.7 g. (45%) of VIII as a colorless liquid, b.p. 85–85.5°, n^{25}D 1.3168. The infrared spectrum contained bands at 5.70 and 5.77 μ. The F^{19} n.m.r. spectrum contained a singlet at +3.01 p.p.m. The proton n.m.r. contained a singlet at +2.28 p.p.m.

Anal. Calcd. for $C_5H_3F_6NO$: C, 29.00; H, 1.47; F, 55.05; N, 6.77. Found: C, 29.07; H, 1.45; F, 54.62; N, 6.37.

No reaction of the imine occurred without boron trifluoride catalyst.

N-Acetylhexafluoroisopropylidenimine, 0.5 g., was dissolved in 5 ml. of 10% sodium hydroxide solution. The solution was then acidified with 5% hydrochloric acid, and the white precipitate that formed was collected on a filter, washed with water, and recrystallized from chloroform. There was obtained 0.3 g. of N-(2-hydroxyhexafluoroisopropyl)acetamide as colorless needles, m.p. 92–93°. This product is identical with the product prepared by the direct reaction of acetamide with hexafluoroacetone.

Hexafluoroacetone–Acetamide Adduct.—A 450-ml. "Hastelloy" bomb charged with 42 g. (0.25 mole) of hexafluoroacetone, 12 g. (0.25 mole) of acetamide, and 25 ml. of ethylene glycol dimethyl ether was heated at 100° for 5 hr. The bomb was cooled and vented, and the liquid contents were evaporated to dryness under reduced pressure at room temperature. The white residue was recrystallized from chloroform to give 34.1 g. (63%) of N-(2-hydroxyhexafluoroisopropyl)acetamide as colorless needles, m.p. 92–93°. The F^{19} n.m.r. spectrum in acetone shows a singlet at +15.7 p.p.m. The infrared spectrum contained bands at 3.07, 6.06, 6.37, and 7.25 μ.

Anal. Calcd. for $C_5H_5F_6NO_2$: C, 26.68; H, 2.24; F, 50.64; N, 6.23. Found: C, 26.84; H, 2.24; F, 50.84; N, 6.43.

2-Aminohexafluoroisopropyl Azide.—A paste of 19.5 g. of sodium azide in 20 ml. of water was stirred vigorously with 120 ml. of cold methylene chloride, and 15 g. of sulfuric acid was added dropwise. The temperature during the entire addition was maintained below 10° by cooling with an ice bath. Sodium sulfate, *ca.* 30 g., was added to dry the mixture, and the methylene chloride solution of hydrazoic acid was decanted into a separate flask and cooled to 0°. Hexafluoroisopropylidenimine, 21 ml. at −10° (*ca.* 0.2 mole), was distilled into this solution, and the reaction mixture was heated to reflux for 18 hr. Distillation gave 21.75 g. (52%) of the azide as a colorless liquid: b.p. 84–85°; n^{25}D 1.3378; infrared at 2.89, 2.95, and 4.67 μ; proton n.m.r. singlet at +2.37 p.p.m.; F^{19} n.m.r. singlet at +13.56 p.p.m.

Anal. Calcd. for $C_3H_2F_6N_4$: C, 17.32; H, 0.97; F, 54.77; N, 26.93. Found: C, 17.62; H, 1.78; F, 54.81; N, 27.03.

3,3-Bis(trifluoromethyl)diaziridine (V).—2-Aminohexafluoroisopropyl azide, 7.3 g. (0.035 mole), contained in a quartz tube open to the atmosphere through a condenser and a drying tube, was irradiated with a low-pressure mercury arc light for 2 days. Large, transparent crystals formed on the side of the tube, and the liquid in the tube became semisolid. The solid was collected on a filter, recrystallized from methylene chloride, and then sublimed at atmospheric pressure. There was obtained 2.7 g. (43%) of V as large transparent prisms, m.p. 80° (sealed capillary). The infrared contained bands at 3.05 and 7.07 μ. The F^{19} n.m.r. spectrum in $CDCl_3$ showed a broad singlet at +2.77 p.p.m. The proton n.m.r. spectrum contained a singlet at +6.74 p.p.m. The mass spectrum showed the most abundant ion at m/e 69 (CF_3^+, 100%) with other major ions at m/e 180 (parent, 24.5%), m/e 112 (75.5%), m/e 29 (62.7%), and m/e 93 (55%).

Anal. Calcd. for $C_3H_2F_6N_2$: C, 20.01; H, 1.12; F, 63.32; N, 15.56. Found: C, 20.17; H, 1.21; F, 63.38; N, 15.61.

Pyrolysis of 2-Aminohexafluoroisopropyl Azide.—2-Aminohexafluoroisopropyl azide, 12.5 g. (0.06 mole), was put dropwise at atmospheric pressure over a period of 1 hr. into a platinum tube 0.5 in. in diameter and 25 in. long, inclined at an angle of 30° and heated to 350° over a length of 12 in. A slow stream of nitrogen (20 ml./min.) was passed through the tube during the pyrolysis. The product, condensed in a strap cooled by an ice–methanol bath, was a mixture of liquid and large, transparent crystals. The crystals were collected on a filter and purified by a series of three atmospheric pressure sublimations at 40°. There was thus obtained 1.18 g. (11% yield) of large colorless crystals, m.p. 80° (sealed capillary), identified as 3,3-bis(trifluoromethyl)diaziridine by comparison of its infrared spectrum with that of a sample prepared by irradiation of the azide. The liquid portion of the reaction mixture was distilled to give 6.5 g. (60% yield) of hexafluoroacetone hydrazone, b.p. 95–96°, identified by comparison of its infrared spectrum with that of an authentic sample of the hydrazone.

Hexafluoroacetone Hydrazone (III, R_f = CF_3).—Hexafluoroisopropylidenimine, 50 ml. at −10° (about 0.5 mole or 82.5 g.), was slowly distilled into a flask containing 16 g. (0.5 mole) of anhydrous hydrazine cooled to 0°. This reaction mixture was then poured into a simple still containing 150 g. of phosphorus pentoxide. The still was heated until no further distillation occurred. The distillate was redistilled through an 18-in. spinning-band column to give 50.8 g. (56% conversion, 68% yield) of hexafluoroacetone hydrazone, b.p. 95.5–96°, n^{25}D 1.3298, and 8.5 ml. (about 14 g., 17%) of recovered imine, b.p. 15–16°. Infrared bands were observed at 2.88, 2.98, and 6.21 μ for NH_2 with a shoulder at ~6.1 μ attributable to C=N. The proton n.m.r. spectrum of the hydrazone shows a broad singlet at +7.35 p.p.m., and the F^{19} n.m.r. spectrum shows two quartets centered at −0.80 and +0.53 p.p.m. The mass spectrum showed the most abundant ion at m/e 69 (CF_3^+, 100%) with other major ions at m/e 180 (parent ion, 55%), 111 (69%), and 93 (19.2%).

Anal. Calcd. for $C_3H_2F_6N_2$: C, 20.01; H, 1.12; F, 63.32; N, 15.56. Found: C, 20.42; H, 1.40; F, 63.04; N, 15.31.

Decafluorodiethyl Ketone Hydrazone.[8]—A 46.5-g. (0.18-mole) sample of 1-(pentafluoroethyl)pentafluoropropylidenimine was mixed with 6.5 ml. of 95% hydrazine at 0°. The suspension was warmed gently with stirring until the mixture became essentially homogeneous. The entire reaction mixture was then poured onto

100 g. of phosphorous pentoxide in a 500-ml. flask. The mixture was warmed at 50-mm. pressure to distil volatile material into a trap cooled at −80°. Fractionation of the material in the trap gave 18.3 g. (39%) of starting imine and 8.1 g. (27% yield) of product, b.p. 122°, $n^{25}\text{D}$ 1.3211. The infrared spectrum showed a doublet for NH_2 at 2.7 and 2.9 μ, an intense band at 6.2 μ ascribed to NH_2 deformation, and a weaker band at 6.1 μ ascribed to C═N. The proton n.m.r. showed a broad peak at +12.8 p.p.m., and the F^{19} n.m.r. showed multiplets at +15.7 (area 3), +17.5 (area 3), +43.3 (area 2), and +50.1 (area 2) p.p.m.

Anal. Calcd. for $C_5H_2F_{10}N_2$: C, 21.44; H, 0.72; F, 67.84; N, 10.01. Found: C, 21.88; H, 0.86; F, 67.95; N, 10.19.

2-H-Hexafluoroisopropylamine.—Hexafluoroisopropylidenimine, 25 g. (15.5 ml. at −10°, 0.15 mole), was slowly distilled into a stirred suspension of 5.0 g. (0.13 mole) of lithium aluminum hydride in 125 ml. of diethylene glycol dimethyl ether cooled in an ice bath. After the addition, the reaction mixture was stirred at room temperature for 1 hr., and then a solution of 15 ml. of water in 30 ml. of diethylene glycol dimethyl ether was cautiously added. The reaction mixture was warmed to 35° under reduced pressure (*ca.* 1 mm.), and the volatile fraction that distilled was condensed in a cold trap. Redistillation gave 14.4 g. (57%) of product as a colorless liquid, b.p. 58–59°, $n^{25}\text{D}$ <1.3. The F^{19} n.m.r. contained a doublet (J = 7 c.p.s.) centered at +9.22 p.p.m. The proton n.m.r. showed two broad peaks at +3.83 and +2.08 p.p.m. with an area ratio of 1:2. The infrared spectrum showed bands at 2.93, 2.99, and 6.12 μ for NH_2 and 3.37 μ for saturated CH.

Anal. Calcd. for $C_3H_3F_6N$: C, 21.57; H, 1.81; F, 68.23; N, 8.38. Found: C, 21.64; H, 1.93; F, 68.00; N, 8.69.

2-H-Hexafluoroisopropylamine Hydrochloride.—Dry hydrogen chloride gas was passed into a solution of 10 g. (0.06 mole) of 2-H-hexafluoroisopropylamine in 200 ml. of dry ether. When no further precipitation occurred, the addition was stopped and the precipitate was collected on a filter, washed with ether, and then recrystallized from dioxane. There was obtained 10.1 g. (83%) of the hydrochloride as white crystals, m.p. 125–130° (with sublimation). The F^{19} n.m.r. spectrum in alcohol showed a doublet (J = 8 c.p.s.) centered at −3.50 p.p.m.

Anal. Calcd. for $C_3H_4ClF_6N$: C, 17.72; H, 1.98; Cl, 17.42. Found: C, 17.36; H, 2.16; Cl, 17.44.

Heptafluoroisopropylamine.—Hexafluoroisopropylidenimine, 1.65 g. (0.01 mole), was mixed with 0.2 g. (0.01 mole) of anhydrous hydrogen fluoride in a polyethylene bottle cooled in an ice bath. An exothermic reaction occurred. The F^{19} n.m.r. spectrum of this product showed a doublet in the CF_3 region and a septet at higher field. Further identification and purification was not attempted since this amine reacts rapidly with glass.

2,2-Bis(trifluoromethyl)-4,5-dimethyl-1,2,3,6-tetrahydropyridine (VI).—A mixture of 5.0 g. (0.03 mole) of hexafluoroisopropylidenimine and 5 ml. of 2,3-dimethylbutadiene was sealed in a Carius tube and heated at 100° for 18 hr. The tube was cooled and opened, and the contents were distilled to give 5.4 g. (74%) of VI as a colorless liquid, b.p. 44° (5 mm.), $n^{25}\text{D}$ 1.3911. The F^{19} n.m.r. showed a singlet at +9.58 p.p.m. The proton n.m.r. contained broad peaks at +1.66 (area 6), +2.33 (area 3), and +3.35 p.p.m. (area 2).

Anal. Calcd. for $C_9H_{11}F_6N$: F, 46.12; N, 5.67. Found: F, 46.19; N, 5.38.

3,3-Bis(trifluoromethyl)-2-azabicyclo[2.2.1]hept-5-ene.—A mixture of 8.25 g. (0.05 mole) of hexafluoroisopropylidenimine and 10 ml. of cyclopentadiene was stirred at room temperature overnight. Distillation gave 7.4 g. (64%) of product as a colorless oil, b.p. 44–45° (10 mm.), $n^{25}\text{D}$ 1.3988. The F^{19} n.m.r. spectrum contained two quartets (J = 11 c.p.s.) centered at −3.51 and +4.52 p.p.m.

Anal. Calcd. for $C_8H_7F_6N$: C, 41.57; H, 3.06; F, 49.32; N, 6.07. Found: C, 41.50; H, 3.45; F, 49.06; N, 6.34.

1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene[1]

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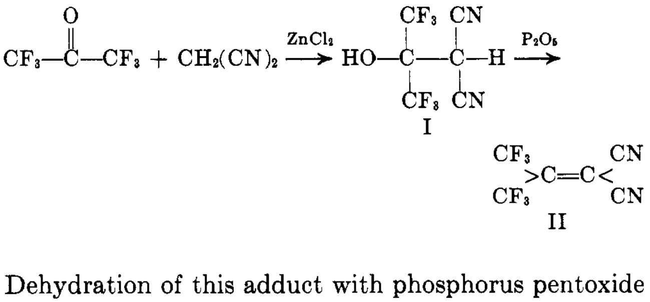
1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene has been prepared from hexafluoroacetone and malononitrile. Reactions of this ethylene are of particular interest for it is both electron poor and highly polarizable. Adducts with dienes, electron-rich olefins, olefins with allylic hydrogens, and nucleophiles are discussed.

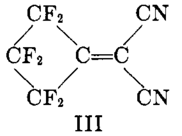
Perfluoro[2] and percyano olefins[3] have received an extensive amount of study. These electron-poor olefins are very active in addition reactions with monoolefins and dienes and are very susceptible to nucleophilic attack. Reactions of olefins that contain both cyano and perfluoroalkyl groups, however, do not appear to have been studied to any great extent. Reactions of unsymmetrically substituted olefins such as 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) would be of particular interest. Like the perfluoro and the percyano olefins, the ethylene would be electron deficient owing to the four electronegative groups attached to the ethylenic carbons. Unlike the perfluoro and percyano olefins, however, II would be highly polarizable, for the geminal cyano groups could stabilize a negative charge at only one end of the double bond in any transition state involving charge separation.

We have discovered a facile synthesis for 1,1-dicyano-2,2-bis(perfluoroalkyl)ethylenes based on the condensation of fluoro ketones with malononitrile. Hexafluoroacetone condenses with malononitrile in the presence of zinc chloride to yield the unstable alcohol I.



$$CF_3-\overset{O}{\overset{\|}{C}}-CF_3 + CH_2(CN)_2 \xrightarrow{ZnCl_2} HO-C(CF_3)_2-C(CN)_2-H \xrightarrow{P_2O_5} (CF_3)_2C=C(CN)_2$$

Dehydration of this adduct with phosphorus pentoxide gives 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene in 50% over-all yield. Dicyanomethylenehexafluorocyclobutane (III) was prepared in a similar manner from malononitrile and hexafluorocyclobutanone.



III

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[1] Portions of this paper were presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

[2] M. Hudlicky, "Chemistry of Organic Fluorine Compounds," The Macmillan Co., New York, N. Y., 1962.

[3] T. L. Cairns and B. C. McKusick, *Angew. Chem.*, **73**, 520 (1961).