1-Ethoxy-9,9-Dichlorobicyclo[6.1.0]nonane (**24**). The reaction of 1-ethoxycyclooctene (25.5 g., 0.166 mole) with ethyl trichloroacetate (38.2 g., 0.195 mole) and sodium methoxide (13.5 g., 0.25 mole) in hexane (250 ml.), under nitrogen was carried out as previously described for the preparation of **3**. There was obtained 10 g. of recovered vinyl ether and 4.3 g. (10.9% of yield) impure 1-ethoxy-9,9-dichlorobicyclo[6.1.0]nonane (b.p. 74–76° at 0.075 mm.).

Anal. Calcd. for $C_{11}H_{18}Cl_2O$: C, 55.68; H, 7.63. Found: C, 56.82; H, 8.05.

The yield of cyclopropane was raised to 28% by employing twice the described quantity of ethyl trichloroacetate and sodium methoxide. The material was refractionated but had the same boiling point and refractive index and essentially the same composition (Found: C, 56.92; H, 8.05). No further purification was attempted.

Reaction of 1-Ethoxy-9,9-dichloro[6.1.0]nonane with Quinoline. A solution of **24** (10.2 g., 0.043 mole) in quinoline (pure, 30 ml.) was heated at the reflux temperature for 25 min.; no strongly exothermic reaction was noted. The mixture was cooled and extracted with a mixture of water and ether. The ether layer was washed with 4% hydrochloric acid until the aqueous wash was distinctly acidic. The ether layer was dried (Na_2CO_3) and distilled. Two principal fractions were collected: (A) b.p. 45–65° at 1 mm., 2.3 g., and (B) 65–67° at 1.0 mm., 0.8 g.

The two fractions were analyzed by vapor phase chromatography using a temperature of 160° on a column (0.25 in. × 10 ft.) packed with Dow Silicon high-vacuum grease (20%) absorbed on Johns-Manville Chromosorb "W" (60–80 mesh). Helium at 45 p.s.i. was used as the carrier gas. The principal component of both fraction A (61.7%) and fraction B (61.3%) was subsequently identified as 1-acetyl-1,3-cycloheptadiene (**25**) (total 1.91 g., 32.7% yield). The other major component of A was cyclooctanone (by infrared and by m.m.p. 32–34°).

Identification of 1-Acetyl-1,3-cycloheptadiene (**25**). The mixture was purified by preparative gas chroma-

tography on the column described in the preceeding section. Minor products, including cyclooctanone, were easily resolved; however, the purest sample of ketone [$\lambda_{max}^{95\% \ EtOH}$ 287 mμ (ϵ 12,070)] showed a shoulder on the v.p.c. curve which was not resolved. The amount of this impurity could not be determined; however, it was a minor one representing approximately 10–15% of the sample.

The n.m.r. spectrum (in CCl_4, τ-units) showed: 3.18 and 3.30 (doublet J = 6.3 c.p.s.; wt. ~1; 2H), 3.72–4.29 (multiplet; wt. ~2; 3 and 4H), 7.92 (singlet, wt. ~3; CH_3—C(=O)—), multiplet centered at 7.57 (wt. ~4, 5 and 7 —CH_2—), multiplet centered at 8.24 (wt. ~2; 6 —CH_2—).

The 2,4-dinitrophenylhydrazone of the ketone [$\lambda_{max}^{CHCl_3}$ 391.5 mμ (ϵ 29,200)] melted at 188.5–189.5° (from ethanol–benzene).

Anal. Calcd. for $C_{15}H_{16}N_4O_4$: C, 56.96; H, 5.10; N, 17.71. Found: C, 56.67; H, 5.22; N, 17.67.

1-Acetylcycloheptane. A sample of the ketone **28** (103 mg.) was reduced in ethyl acetate (10 ml.) using 10% Pd–C (8.6 mg.) as catalyst. The catalyst and solvent were removed and the residue was converted to the semicarbazone (m.p. 175–176.5°, from ethanol–water).

Authentic 1-acetylcycloheptane was prepared[17] as previously described. The semicarbazone prepared from the authentic ketone was identical (m.p. and m.m.p. 175–176°) with that prepared from **25**.

Tropone. Reaction of 1-Ethoxy-1,3,5-cycloheptatriene with Selenious Acid. A mixture of **5** (0.50 g., 0.0037 mole) and selenious acid (0.50 g., 0.0039 mole) in absolute ethyl alcohol (15 ml.) was heated at the reflux temperature for 21 hr. The solution was filtered and then methanol was removed to leave 0.47 g., $n^{25}D$ 1.5605) of crude tropone (reported[23] $n^{25}D$ 1.6070). The ultraviolet spectrum of the residue showed the characteristic spectrum of tropone.[24] The yield of tropone was ~38% based on absorbance at 228, 231.5, 224, and 312.5 mμ.

(23) W. von E. Doering and F. L. Detert, *J. Am. Chem. Soc.*, 73, 877 (1951).
(24) H. J. Dauben, H. J. Ringold, *ibid.*, 73, 876 (1951).

Organic Fluoronitrogens. II.
The Reductive Defluorination Reaction[1]

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Contribution No. 303 from the Central Research Laboratories, Minnesota Mining and Manufacturing Company, St. Paul 19, Minnesota. Received August 21, 1964

The reductive defluorination of perfluoramines with dicyclopentadienyliron or dicumenechromium is described. Difluoramino compounds are converted either to the perfluorimine or perfluoronitrile by the proper selection of organometallic reducing agent. High conversions to perfluoroazomethines can also be realized by reaction of perfluoroacyclic or -cyclic secondary fluoramines with dicyclopentadienyliron.

Introduction

The increased interest in the fluorocarbons in the last decade has led to the discovery of several new and im-

portant classes of compounds. In these studies, a few fluorocarbons which contain fluorine bonded to nitrogen have been described. It has been generally recognized that these types of compounds are somewhat inert and often exhibit the thermal stability characteristics approaching the fluorocarbons themselves. As a result of the inherent oxidizing capabilities and the relative thermal stability of the NF group, the nitrogen–fluorine compounds often do not react at all or react to too great an extent. It should be pointed out that not only is the number of nitrogen–fluorine compounds in the literature extremely small but also that their chemical reactions, other than pyrolysis, have generally not been elucidated. One of the most striking and characteristic reactions of nitrogen–fluorine compounds which has been observed is the oxidation of potassium iodide. For this reason it was considered promising to examine the oxidative reactions of nitrogen–fluorine compounds employing reducing agents soluble in nonprotonic solvents.

The present paper reports the reactions of perfluoramines with "sandwich" bonded organometallic reducing agents as general, convenient, one-step routes to perfluorimines, -nitriles, and -azomethines. Perfluorimines and -azomethines have been prepared by the pyrolysis of secondary[2a,b] and tertiary[3,4] perfluoroalkylamines, fluorocarbon carbamyl fluorides,[5] and oxazetidines,[6,7] by elimination of hydrogen fluoride from fluorocarbon-N-hydroamines,[4] by the action of nitrogen trifluoride on perfluoroolefins and -nitriles,[8] and as fluorination products.[9–13]

Results and Discussion

The reductive defluorination reaction described here, in which dicyclopentadienyliron (ferrocene) or dicumenechromium act primarily as reducing agents, serves to introduce a $>C=N-$ or $-C\equiv N$ moiety into the fluorocarbon structure in high yield. The use of these reagents is especially convenient since they permit the use of nonprotonic halocarbon solvents at room temperature.

Additional driving force is supplied to the reaction by the oxidation of the soluble, neutral organometallic reagent to the cationic species which precipitates from the solution as a salt. Further, the aforementioned oxidation is also accompanied by a color change which thus serves as a measure of the extent of completion of the reaction. In the oxidation of the soluble, orange-colored dicyclopentadienyliron (ferrocene), for example,

(2) (a) J. A. Attaway, R. H. Groth, and L. A. Bigelow, *J. Am. Chem. Soc.*, 81, 3599 (1959); (b) B. C. Bishop, J. B. Hynes, and L. A. Bigelow, *ibid.*, 84, 3409 (1962).

(3) W. H. Pearlson and L. J. Hals, U. S. Patent 2,643,267 (1953).

(4) K. A. Petrov, *J. Gen. Chem. USSR*, 29, 2662 (1959).

(5) J. A. Young, T. C. Simmons, and F. W. Hoffmann, *J. Am. Chem. Soc.*, 78, 5637 (1956).

(6) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1881 (1955).

(7) D. A. Barr and R. N. Haszeldine, *ibid.*, 3416 (1956).

(8) R. D. Dresdner, F. N. Tlumac, and J. A. Young, *J. Am. Chem. Soc.*, 82, 5831 (1960).

(9) R. N. Haszeldine, *Research* (London), 4, 338 (1951).

(10) J. B. Hynes and L. A. Bigelow, *J. Am. Chem. Soc.*, 84, 2751 (1962).

(11) J. B. Hynes, B. C. Bishop, P. Bandyopadhyay, and L. A. Bigelow, *ibid.*, 85, 83 (1963).

(12) B. C. Bishop, J. B. Hynes, and L. A. Bigelow, *ibid.*, 85, 1606 (1963).

(13) H. Ulrich, E. Kober, H. Schroeder, R. Rätz, and C. Grundmann, *J. Org. Chem.*, 27, 2585 (1962).

the ferricinium salt which precipitates from solution is blue-green.

This reaction has been found to be applicable for acyclic and cyclic difluoramines, acyclic and cyclic monofluoramines, as well as compounds possessing a multiplicity of nitrogen–fluorine bonds. Vapor phase chromatographic analysis of each reaction mixture has also indicated that the level of unknown side products is very low.

Difluoramines. A typical difluoramino compound, perfluoro-1-azapentane (I), was treated with 2 moles of dicyclopentadienyliron in carbon tetrachloride at room temperature producing perfluoro-1-azapentene-1 (II) in high yield. Identification of the product as

$$C_3F_7CF_2NF_2 \xrightarrow{(C_5H_5)_2Fe} C_3F_7CF=NF$$
$$\quad\quad I \quad\quad\quad\quad\quad\quad\quad\quad II$$
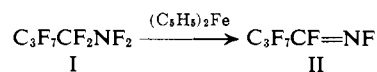
perfluoro-1-azapentene-1 (II) was accomplished by elemental and spectral analyses. A broad F^{19} nuclear magnetic resonance absorption peak which can be assigned with some confidence to the fluorimino moiety appears at $+14.4$ ϕ^*.[14] The single carbon-fluorine adjacent to the fluorimino group shows the expected doublet at $+77.0$ ϕ^* ($J = 36.3$ c.p.s.) attributed to spin–spin coupling with the $=NF$. Further splitting into a triplet of triplets ($J = 12.0$ and 6.0 c.p.s.) arising from coupling with the two different CF_2 groups is indicated. Infrared spectral evidence for the $>C=NF$ structure is supplied by an absorption at 5.92 μ.

In a similar manner, 1,1-dichloroperfluoro-3-azapropane (III) yields 1,1-dichloroperfluoro-3-azapropene-2 (IV) on reaction with dicyclopentadienyliron. An

$$CFCl_2CF_2NF_2 \xrightarrow{(C_5H_5)_2Fe} CFCl_2CF=NF$$
$$\quad\quad III \quad\quad\quad\quad\quad\quad\quad IV$$
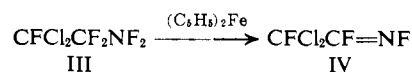
absorption at 5.95 μ in the infrared spectrum and a peak at $+21.5$ ϕ^* in the F^{19} nuclear magnetic resonance spectrum are assigned to the fluorimino moiety. The single carbon–fluorine adjacent to the fluorimino group appears as a doublet at 77.2 ϕ^* ($J = 31.9$ c.p.s).

In a manner analogous to the formation of II and IV, 1-fluoriminoperfluorocyclohexane (VI) is the product, obtained in high yield, from the reaction of dicyclopentadienyliron with 1-difluoraminoperfluorocyclohexane (V).
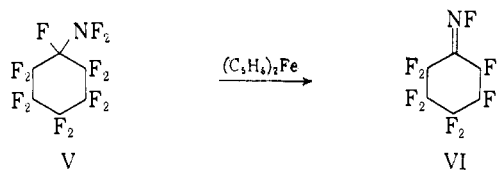
Elemental and spectral analyses have been employed to establish the structure of VI. The $>C=NF$ group exhibits a medium absorption at 6.07 μ in the infrared and a poorly resolved triplet ($J = 57$ c.p.s.) at -52.4 ϕ^* in the F^{19} n.m.r. spectrum. It is to be expected that the absorption peak positions and spin–spn coupling constants of the CF_2 groups *syn* and *anti* to the fluorimino moiety would be different. Thus, the doublet ($J = 57$ c.p.s.) at $+114.5$ ϕ^* is assigned to the CF_2 *syn* to the NF, and the absorption with no resolved splitting

(14) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, 63, 761 (1959).

at $+118.8 \phi^*$ is assigned to the CF_2 *anti* to the NF. Although arbitrary, these assignments were made after consideration of the spin–spin coupling in perfluoro-olefins. In perfluoropropene, for example, the coupling constant for the *cis* ($CF–CF_3$) interaction is almost three times as large as that observed for the *trans* ($CF–CF_3$) interaction.[15]

The reductive defluorination of a bis(difluoramino)-fluorocarbon, perfluoro-1,5-diazapentane (VII), was effected with 6 moles of dicyclopentadienyliron in bis-(trifluoromethyl)benzene at room temperature. The

$$NF_2CF_2CF_2CF_2NF_2 \xrightarrow{(C_5H_5)_2Fe} FN{=}CFCF_2CF{=}NF$$
$$\text{VII} \qquad\qquad\qquad \text{VIII}$$
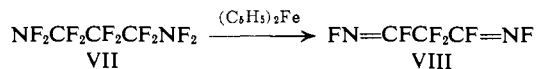
identity of the product, perfluoro-1,5-diazapenta-1,4-diene (57% yield), was established by elemental and spectral analyses. A broad F^{19} nuclear magnetic resonance absorption peak at $+14.9 \phi^*$ and a band of medium intensity at 5.93μ in the infrared are assigned to the fluorimino moiety. The single carbon–fluorine groups of VIII appear as a doublet at $+79.6 \phi^*$ ($J = 38.5$ c.p.s.) attributed to spin–spin coupling with the $=$NF.

When properly applied, the reaction described herein has excellent preparative value since the use of dicyclopentadienyliron specifically yields the fluorimino derivative. The reduction stops at this intermediate stage presumably because the oxidizing power of the fluorimino moiety is less than that of the difluor-amino group and is not sufficient to react with dicyclopentadienyliron. However, dicumenechromium, an organometallic which is known to be a better reducing agent than dicyclopentadienyliron, effects the further reduction of acyclic fluorocarbon difluoramines and fluorimines to perfluoronitriles in high yields.

Formation of Perfluoronitriles. Perfluoro-*n*-butyro-nitrile (IX) was formed in 96% yield by the action of dicumenechromium on perfluoro-1-azapentane (I).

$$C_3F_7CF_2NF_2 \xrightarrow{(C_9H_{12})_2Cr} C_3F_7C{\equiv}N$$
$$\text{I} \qquad\qquad\qquad \text{IX}$$
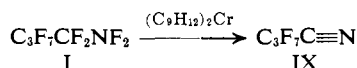
The identity of IX was established by spectral comparisons with an authentic sample.

The reaction of dicumenechromium was carried out quantitatively. It was found that 2.5 moles of dicumenechromium per mole of I afforded the following product distribution: 21.4% perfluoro-1-azapentene-1 (II), 28% perfluoro-*n*-butyronitrile (IX), and 50% unreacted I. On the other hand, 4.5 moles of dicumenechromium resulted in a 96% conversion to IX. It is evident that this reaction is a four-electron change involving the oxidation.

$$(C_9H_{12})_2Cr \longrightarrow (C_9H_{12})_2Cr^+ + e^-$$
$$\text{red-brown} \qquad\qquad \text{yellow}$$
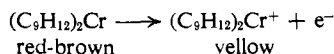
Secondary Monofluoramines. The reductive defluor-ination reaction described here is not limited to difluor-amino compounds; in fact, it is more facile with second-ary perfluoramines. The reaction of perfluoro-3-aza-pentane (X) with dicyclopentadienyliron to afford the previously reported[3] perfluoro-3-azapentene-2 (XI) was complete in only 2 hr. compared to reaction times of 6–14 days for the difluoramino reactants.

(15) H. M. McConnell, C. A. Reilly, and A. D. McLean, *J. Chem. Phys.*, 24, 479 (1956).

$$C_2F_5NC_2F_5 \xrightarrow{(C_5H_5)_2Fe} C_2F_5N{=}CFCF_3$$
$$\quad\ |\ \ F$$
$$\text{X} \qquad\qquad\qquad \text{XI}$$
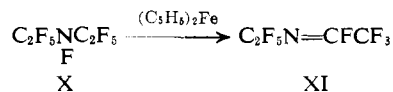
Spectroscopically, azomethine XI was identical with an authentic sample prepared by the pyrolysis of per-fluorotriethylamine.[3]

A typical cyclic monofluoramine, perfluoro-1-aza-cyclohexane (XII), was treated with 2 molar equiv. of dicyclopentadienyliron to produce the recently re-ported[13] compound, perfluoro-1-azacyclohexene-1 (XIII).
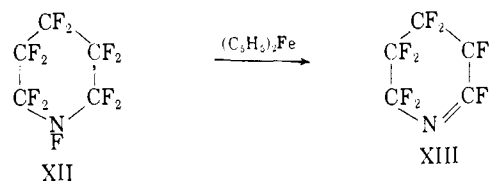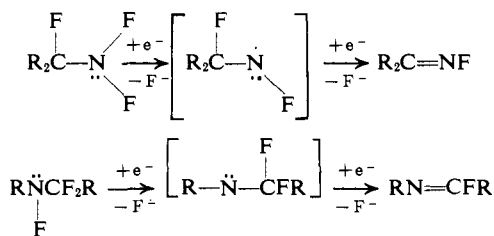

Elemental and spectral analyses and molecular weight determinations leave little doubt as to the structure of XIII. The infrared spectrum of perfluoro-1-azacyclo-hexene-1 clearly exhibits a strong $>C{=}N-$ stretching absorption at 5.69μ. The F^{19} n.m.r. spectrum of XIII shows only a slight similarity to that of XII. A broad unresolved peak at $+93.0 \phi^*$ is in the region for a $-CF_2$ group bonded to the $-N{=}C<$ moiety (compare with $-CF_2-N{=}C<$ at $+98.5 \phi^*$ in XI). The single carbon-fluorine absorption peak is a poorly resolved triplet ($J = 25$ c.p.s.) at $+51.8 \phi^*$, while the $-CF_2$ group adjacent to it appears as a doublet ($J \cong 27$ c.p.s.) at $+122.1 \phi^*$.

The reductive defluorination of a cyclic fluoramine having a multiplicity of nitrogen–fluorine groups has also been carried out. Cyanuric fluoride (XV) was formed in high yield by the reaction of dicyclopenta-dienyliron with perfluoro-1,3,5-triazacyclohexane (XIV). Chromatographic separation of the mixture indicates the reaction, involving a six-electron change, was essentially free of side products. Spectroscopically XV
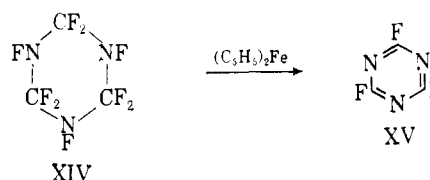

was identical with an authentic sample of cyanuric fluoride.

Mechanism Considerations. Although no detailed mechanistic study was undertaken, it is possible to formulate reasonable reaction paths for the formation of the products by way of a common initiation step, the one-electron reduction of the nitrogen–fluorine bond. The general stoichiometry of the reaction in-
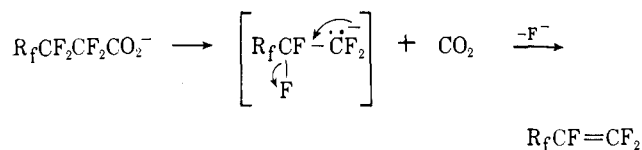

dicates a two-electron change over-all. The second electron change leading to the elimination of the α-

fluorine as an anion is believed to be concerted, perhaps involving a transient nitrogen–anion intermediate of the type

$$R_2C\overset{\frown}{-}\overset{\cdot\cdot}{N}\overset{-}{F}$$
$$\overset{|}{\underset{F}{}}$$
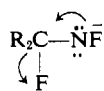
A somewhat similar perfluorocarbanion intermediate has been postulated[16] in the decarboxylation reaction

$$R_fCF_2CF_2CO_2^- \longrightarrow \left[R_fCF\overset{\frown}{-}\overset{\cdot\cdot}{C}F_2 \atop \overset{|}{\underset{F}{}} \right] + CO_2 \xrightarrow{-F^-}$$

$$R_fCF{=}CF_2$$

leading to perfluoroolefins.

A logical extension of the above is submitted to rationalize the conversion of difluoramines to nitriles, having previously demonstrated the fluorimine as being an intermediate.

$$R_fCF{=}NF \xrightarrow[-F^-]{+e^-} R_f\overset{\cdot}{C}{=}\overset{\cdot\cdot}{N} \xrightarrow[-F^-]{+e^-} R_fC{\equiv}N$$
$$\overset{|}{\underset{F}{}}$$
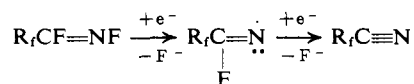
Experimental

Materials. The dicyclopentadienyliron was purchased from Eastern Chemical Corp., Newark, N. J., and resublimed before use.

Dicumenechromium was obtained from the Union Carbide Chemical Co., New York, N. Y.

The preparation of perfluoro-1-azapentane (I) has been reported in the literature.[12] The purified material, b.p. 30.5°, mol. wt. 270 (lit.[12] 29.5°), exhibited the infrared absorption spectrum recorded below, and F^{19} n.m.r. spectrum as assigned in Table I; infrared absorptions: 7.34 (m), 7.77 (s), 8.04 (vs), 8.34 (s), 8.56 (m), 8.72 (s), 10.15 (m), 10.60 (s), 11.25 (s), 12.07 (m), 12.64 (m), and 13.56 (s) μ.

Perfluoro-3-azapentane (X) is available from the electrochemical fluorination[17] of the hydrocarbon analog. Fractional distillation yielded a mixture of the structural isomers $(CF_3)_2NC_2F_5$ and X. Finally, a preparative scale chromatographic separation yielded X in 94% purity, mol. wt. 269, b.p. 26°. The F^{19} n.m.r. (Table I) and infrared spectra are consistent with the assigned structure: infrared absorptions: 7.37 (m), 8.03 (vs), 8.40 (vs), 8.87 (m), 9.06 (s), 9.22 (m), 13.60 (m), and 14.31 (s) μ.

The electrofluorination of pyridine leading to perfluoro-1-azacyclohexane (XII) has been reported in the literature.[18] The purified material, b.p. 48.7–49°, mol. wt. 283 (lit.[18] b.p. 49.5°), was analyzed by vapor phase chromatography and a purity of not less than 99% was indicated. The F^{19} n.m.r. and infrared spectra are listed in Table I and below, respectively; infrared absorptions: 7.53 (s), 7.73 (vs), 7.84 (vs), 8.05 (s), 8.21 (vs), 8.50 (vs), 9.32 (s), 9.70 (s), and 10.36 (vs) μ.

Fluorination of aniline in the electrochemical cell leading to the preparation of 1-difluoraminoperfluorocyclohexane (V) has been described by Simons.[19] A

(16) R. N. Haszeldine, *Nature*, **168**, 1028 (1951).
(17) J. H. Simons, U. S. Patent 2,519,983 (1950).
(18) T. C. Simmons and F. W. Hoffmann, *J. Am. Chem. Soc.*, **79**, 3429 (1957).
(19) J. H. Simons, U. S. Patent 2,490, 099 (1949).

boiling point range of 76–78° (lit.[19] 77°), as well as infrared and F^{19} n.m.r. spectra are recorded for the purified material obtained by vapor phase chromatography; infrared absorptions: 7.57 (s), 7.81 (vs), 7.96 (vs), 8.11 (vs), 8.35 (vs), 8.64 (m), 9.47 (s), 9.84 (s), 10.05 (vs), 11.76 (vs), and 13.14 (m) μ.

The preparation of perfluoro-1,3,5-triazacyclohexane (XIV) has been reported.[10] Purification was accomplished by simple distillation followed by isolation of the pure material, b.p. 48.5° (lit.[10] 51°), by vapor phase chromatography. The F^{19} n.m.r. spectrum of XIV (Table I) and the infrared spectrum which exhibited bands at 7.55 (s), 7.82 (vs), 8.03 (vs), 8.41 (vs), 9.33 (s), 9.81 (m), 10.54 (vs), and 10.83 (s) μ are in agreement with the reported values.[10]

Chromatographic analyses were performed with a Model 154D Perkin-Elmer vapor fractometer, utilizing fluorocarbon type stationary phases. The analytical analyses as recorded in Table II were obtained using 0.25-in. o.d. tubes, 2 m. long and packed with a nitrosotrifluoromethane–tetrafluoroethylene copolymer on Celite. For the most part, the preparative scale separations were done on a larger unit employing 0.5-in. o.d. tubes, 6 m. long and packed with FX-45 (Minnesota Mining and Manufacturing Co.), or 0.5-in. o.d. tubes, 2 m. long packed with Kel-F tetramer oil (FC-8126), on acid-washed Celite. As a result of the lower volatility of 1-difluoraminoperfluorocyclohexane (V), the preparative separations were more efficiently carried out at 80° on a 0.5-in. o.d., 2-m. length unit packed with Kel-F pentamer on Celite.

Infrared spectra were run on a Perkin-Elmer Model 21 double beam instrument using a 2.5-cm. gas cell with NaCl windows. Nuclear magnetic resonance spectra were made with a Varian V-4300-2 instrument operating at 40.0 Mc. and utilizing an internal standard of $CFCl_3$ for the determination of chemical shifts. The values are reported in ϕ^* values[14] at a dilution of about 25%, negative values for low field. Trifluoroacetic acid is 76.5 ϕ^* on this scale.

Procedure. In general, two experimental procedures were employed, the choice of which depended upon the reactivity and volatility of reactant and product.

a. Procedure a employing more conventional halocarbon solvents was used for both difluoramino and secondary fluoramino compounds. Trichlorofluoromethane was utilized for reactants of low volatility and either carbon tetrachloride or bis(trifluoromethyl)benzene for those exhibiting high volatility, *i.e.*, b.p. <35°. In either case, the dicyclopentadienyliron was weighed out into an ampoule and solvent added. After degassing, the difluoramino reactant was condensed into the ampoule at liquid nitrogen temperature by appropriate vacuum transfer techniques. The sealed ampoule was either periodically shaken or stirred while at room temperature. Separation of the reductive-defluorination reaction mixture was accomplished by vapor phase chromatography employing the usual trapping techniques.

b. Procedure b was very convenient for the reactions of the secondary fluoramino compounds on the millimole level. It is recommended, however, that for larger scale reactions, procedure a be used with suitable modifications to permit adequate stirring.

In procedure b, a paste of dicyclopentadienyliron and

Table I. F^{19} Nuclear Magnetic Resonance Spectra

Formula	No.	Group	ϕ^*	Group	ϕ^*
1. Acyclic					
$\overset{a}{C}F_3\overset{b}{C}F_2CF_2\overset{c}{C}F_2NF_2$	I	CF₃	+81.4	CF₂(c)	+116.0
		CF₂(a)	+126.8	NF₂	−16.7
		CF₂(b)	+124.0		
$\overset{a}{C}F_3\overset{b}{C}F_2CF_2CF{=}NF$	II	CF₃	+81.1	=CF−	+77.0
		CF₂(a)	+126.9	=NF	+14.4
		CF₂(b)	+118.8		
CFCl₂CF₂NF₂	III	CFCl₂	+72.8	NF₂	−20.7
		CF₂	+113.8		
CFCl₂CF=NF	IV	CFCl₂	+68.3	=NF	+21.5
		=CF−	+77.2		
$NF_2\overset{a}{C}F_2\overset{b}{C}F_2CF_2NF_2$	VII	CF₂(a)	+123.7	NF₂	−17.0
		CF₂(b)	+116.1		
FN=CFCF₂CF=NF	VIII	CF₂	+110.7	=NF	+14.9
		=CF−	+79.6		
(CF₃CF₂)₂NF	X	CF₃	+83.2	NF	+93.1
		CF₂	+109.5		
$\overset{a}{C}F_3\overset{b}{C}F_2N{=}CFCF_3$	XI	CF₃(a)	+86.7	CF₂	+98.5
		CF₃(b)	+74.5	=CF−	+29.3
2. Cyclic					
(structure b,c CF₂CF₂ / CF₂ / NF / CF₂CF₂)	XII	CF₂(a)	+133.4	CF₂(c)	+109.1
		CF₂(b)	+131.2	NF	+112.2
(structure b,a CF₂CF₂ / CF₂ / N / c CF₂CF d)	XIII	CF₂(a)	+93.0	CF₂(d)	+122.1
		CF₂(b)ᵃ	+134.4	=CF−	+51.8
		CF₂(c)	+135.6		
(structure b,c CF₂−CF₂ / CF₂ / C−NF₂ / CF₂−CF₂ / F)	V	CF₂(a-ax)ᵇ,ᶜ	125.4	CF	173.3
		(a-eq)ᵈ	142.0		
		CF₂(b-ax)ᶜ	123.5	NF₂	−24.4
		(b-eq)ᵈ	140.5		
		CF₂(c-ax)ᶜ	119.5		
		(c-eq)ᵈ	131.3		
(structure d,e CF₂CF₂ / c CF₂ / C=N / CF₂CF₂ / F, b a)	VI	CF₂(a)	+114.5	CF₂(b,c,d)ᵉ	+133.7
		CF₂(e)	+118.8	=NF	−52.4
(structure NF−CF₂ / CF₂ / NF / NF−CF₂)	XIV	CF₂	+89.2	NF	+87.9
(structure N−CF / CF / N / N=CF)	XV	CF	+31.1		

ᵃ CF₂(b) and CF₂(c) are assigned arbitrarily and may be reversed. ᵇ Indicated values are from AB type pattern analysis (J_{AB} = 290 c.p.s.). Axial fluorine atoms are probably the lower values, but this is not certain. For a discussion of this type pattern analysis see G. V. D. Tiers, *Proc. Chem. Soc.*, 391 (1960); J. Feeney and J. H. Sutcliffe, *Trans. Faraday Soc.*, **56**, 1559 (1960). ᶜ ax = axial. ᵈ eq = equatorial. ᵉ Broad and complex pattern around + 133.7 ϕ^*; unsymmetrical, with stronger absorption on the low side of the indicated position.

Table II. Relative Retention Times of Nitrogen Fluorocarbons

Nitrogen–fluorine compd.		Reductive–defluorination product	
Compd.	$T_R{}^a$	Compd.	T_R
C₄F₉NF₂ (I)	73.4	C₃F₇CF=NF (II)	57.1
		C₃F₇C≡N (IX)	24.5
CFCl₂CF₂NF₂ (III)	121.5	CFCl₂CF=NF (IV)	92.0
CF₂(CF₂)₄CFNF₂ (V)	418	CF₂(CF₂)₄C = NF (VI)	296
NF₂(CF₂)₃NF₂ (VII)	128.8	FN=CFCF₂CF = NF (VIII)	61.4
C₂F₅NFC₂F₅ (X)	47.0	C₂F₅N=CFCF₃ (XI)	34.6
CF₂(CF₂)₄NF (XII)	130	CF₂(CF₂)₃N=CF (XIII)	97.8
CF₂NFCF₂NFCF₂NF (XIV)	154	N=CFN=CFN=CF (XV)	182

ᵃ $T_R = (T_{compd} - T_{air})/(T_{CCl_4} - T_{air}) \times 100$; CCl₄ = 100.0.

FC-8126 (Kel-F tetramer) was coated on the walls of an ampoule fitted with a 24/40 joint and stopcock. After degassing, the nitrogen-fluorine compound was condensed into the reactor. Visually, the reaction was complete in a few hours at ice-bath temperature. The volatile products were purified as in procedure a.

Perfluoro-1-azapentene-1 (*II*). A 0.251-g. (9.25 × 10⁻⁴ mole) sample of perfluoro-1-azapentane (I) was allowed to react for 6 days with 0.371 g. (1.99 × 10⁻³ mole) of dicyclopentadienyliron in 1.5 ml. of carbon tetrachloride by procedure a. A vapor phase chromatogram of the mixture indicated 82.2% conversion to perfluoro-1-azapentene-1 (II) boiling at 22°.

A medium absorption at 5.92 μ (C=N) was evident in the infrared spectrum, as well as the following bands: 7.25 (m), 7.28 (m), 7.53 (m), 7.79 (m), 8.03 (vs), 8.30 (s), 8.69 (s), 8.88 (m), 9.19 (m), 10.11 (m), 10.63 (s), 10.85 (s), 12.12 (s), and 13.37 (s) μ. The F¹⁹ nuclear magnetic resonance spectrum is recorded in Table I.

Anal. Calcd. for C_4F_9N: C, 20.6; F, 73.4; N, 6.0; mol. wt., 233. Found: C, 20.4; F, 72.2; N, 6.0; mol. wt., 230.

1,1-Dichloroperfluoro-3-azapropene-2 (*IV*). Procedure a was utilized with 0.204 g. (1 × 10⁻³ mole) of 1,1-dichloroperfluoro-3-azapropane (III)[20] and 0.558 g. (3 × 10⁻³ mole) of dicyclopentadienyliron in 7 ml. of bis(trifluoromethyl)benzene solvent for 2 weeks. Separation of the reaction mixture by vapor phase chromatography afforded 3.4 × 10⁻⁴ mole (34% yield) of pure IV exhibiting bands at 5.95 (m), 7.53 (m), 8.78 (s), 9.20 (m), 10.00 (m), 10.46 (m), 10.84 (m), 11.67 (s), and 12.60 (s) μ in the infrared spectrum.

Anal. Calcd. for $C_2Cl_2F_3N$: C, 14.5; F, 34.3; mol. wt., 166. Found: C, 14.5; F, 34.2; mol. wt., 168.

Perfluoro-1,5-diazapenta-1,4-diene (*VIII*). Utilizing procedure a, 1.12 g. (6 × 10⁻³ mole) of dicyclopentadienyliron in 10 ml. of bis(trifluoromethyl)benzene was allowed to react for 2 weeks with 0.254 g. (1 × 10⁻³ mole) of perfluoro-1,5-diazapentane (VII).[20] Separation of the reaction mixture by fractional distillation-condensation and vapor phase chromatography afforded 5.7 × 10⁻⁴ mole (57% yield) of pure VIII. The infrared spectrum was characterized by absorptions at 5.93 (m), 7.30 (m), 7.48 (m), 8.54 (s), 8.76 (m), 9.43 (m), 10.32 (s), 10.54 (s), 11.48 (w), 12.40 (s), and 14.60 (w) μ.

Anal. Calcd. for $C_3F_6N_2$: C, 20.2; F, 64.0; mol. wt., 178. Found: C, 19.9; F, 63.9; mol. wt., 181.

Perfluoro-n-butyronitrile (*IX*). Utilizing procedure a, 2.6 g. (9.0 × 10⁻³ mole) of dicumenechromium (dry nitrogen atmosphere) in 2 ml. of bis(trifluoromethyl)-benzene was allowed to react for 15 hr. with 0.54 g. (2.0 × 10⁻³ mole) of I. A chromatographic analysis of the reaction mixture indicated 96.1% conversion to perfluoro-n-butyronitrile (IX) (mol. wt., 195 (calcd. for C_4F_7N); 193 (found)). The infrared absorption spectrum of IX exhibited a medium band at 4.43 μ (-C≡N) and was superimposable on that of an authentic sample of perfluoro-n-butyronitrile.

Perfluoro-3-azapentene-2 (*XI*). A sample of perfluoro-3-azapentane (X) weighing 0.678 g. (2.5 × 10⁻³ mole) was allowed to react with 0.93 g. (5.0 × 10⁻³ mole) of dicyclopentadienyliron using procedure b. After 2

(20) The author is indebted to Drs. B. C. Bishop, J. B. Hynes, and L. A. Bigelow for samples of 1,1-dichloroperfluoro-3-azapropane (III) and perfluoro-1,5-diazapentane (VII).

hr., gas-liquid chromatography indicated 84.2% conversion to perfluoro-3-azapentene-2 (XI), b.p. 14° (lit.[3] 13-13.5°), mol. wt. 232. The F¹⁹ n.m.r. (Table I) and presence of strong absorption at 5.58 μ (>C=N-) as well as bands at 7.46 (s), 8.04 (vs), 8.23 (vs), 8.33 (vs), 9.00 (m), 9.14 (m), 9.31 (m), 11.75 (m), 14.35 (m), and 14.96 (m) μ in the infrared spectrum confirm the structure. The infrared spectrum was identical with that of the product obtained by pyrolysis of perfluorotriethylamine.

Perfluoro-1-azacyclohexene-1 (*XIII*). Procedure b was employed with 1.0 g. (3.54 × 10⁻³ mole) of perfluoro-1-azacyclohexane (XII) and 1.49 g. (8.0 × 10⁻³ mole) of dicyclopentadienyliron. After 2 hr., the volatile reaction mixture was separated by chromatography. The conversion to XIII was 93.8% as measured by peak areas. Perfluoro-1-azacyclohexene-1 (b.p. 43°) exhibits bands at 5.69 (>C=N-), 7.36 (m), 7.58 (m), 8.00 (s), 8.30 (s), 8.58 (s), 9.74 (s), and 10.40 (s) μ in the infrared spectrum and F¹⁹ n.m.r. as recorded in Table I.

Anal. Calcd. for C_5F_9N: C, 24.5; F, 69.8; N, 5.7; mol. wt., 245. Found: C, 24.1; F, 69.0; N, 5.5; mol. wt., 241.

1-Fluoriminoperfluorocyclohexane (*VI*). The fluorimino compound (VI) was obtained in 78% conversion by procedure a after 7 days by the reaction of 1.49 g. (8.0 × 10⁻³ mole) of dicyclopentadienyliron in 5 ml. of fluorotrichloromethane on 1.33 g. (4.0 × 10⁻³ mole) of 1-difluoraminoperfluorocyclohexane (V). In this case, preliminary separation of VI from the solvent was accomplished by fractional distillation-condensation techniques, then chromatography. It seems clear that the medium absorption peak at 6.07 μ in the vapor spectrum of 1-fluoriminoperfluorocyclohexane (b.p. 64°) is in the region for >C=N- stretching. Other peaks appear at 7.63 (vs), 7.90 (s), 8.13 (m), 8.30 (vs), 8.50 (m), 8.96 (m), 9.96 (vs), 10.72 (vs), and 11.78 (m) μ. The F¹⁹ n.m.r. spectrum, discussed in some detail elsewhere in this paper, is recorded in Table I.

Anal. Calcd. for $C_6F_{11}N$: C, 24.4; F, 70.8; N, 4.7. Found: C, 24.3; F, 69.8; N, 4.6.

Cyanuric Fluoride (*XV*). A 0.050-g. (2.01 × 10⁻⁴ mole) sample of perfluoro-1,3,5-triazacyclohexane (XIV) was allowed to react with 0.223 g. (1.2 × 10⁻³ mole) of dicyclopentadienyliron by procedure b. A vapor phase chromatogram of the volatile reaction products after 18 hr. indicated 96.5% conversion to cyanuric fluoride (XV). The infrared absorption spectrum of XV was superimposable on that of an authentic sample of cyanuric fluoride and exhibited characteristic absorption bands at 6.18 (vs), 6.33 (vs), 7.03 (vs), 9.19 (s), and 12.18 (m) μ.