Anal. Calcd for $C_{14}H_8F_4N_2$: C, 60.05; H, 2.88; N, 10.01. Found: C, 61.51; H, 2.96; N, 9.89.

9,10-Dichloro-9,10-bis(difluoramino)-9,10-dihydroanthracene (IIc and IIc).—In a 240-ml tube containing 30 g (0.12 mole) of 9,10-dichloroanthracene and 60 g of benzene was condensed 14.0 g (0.135 mole) of N_2F_4, and the tube was sealed and shaken at 71° for 1 hr. The benzene-insoluble solid was unreacted 9,10-dichloroanthracene and was removed by filtration. The benzene solution was evaporated *in vacuo* to give 23.0 g (54%) of 9,10-dichloro-9,10-bis(difluoramino)anthracene as a mixture of *cis* and *trans* isomers. It was carefully recrystallized from petroleum ether (40–60°)-benzene with the minimum of heating to give 20 g of white, cubic crystals: mp 120–125° dec; infrared maxima (Nujol), 10.17 (m), 10.57 (s), 11.32 (s), 11.57 (sh) (m), 11.72 (sh) (m) (NF_2), and 13.40 (s) μ (aromatic); ultraviolet absorption (EtOH), 273 mμ (ϵ 1600), 280 (1490), 298 (157), 309 (100), 332 and (42.5); F^{19} nmr (nitrobenzene), −6175 cps and −6075 cps (NF_2) in about 2:1 ratio.

Anal. Calcd for $C_{14}H_8Cl_2F_4N_2$: C, 47.90; H, 2.30; Cl, 20.20; F, 21.65; N, 7.98. Found: C, 48.39; H, 2.59; Cl, 20.16; F, 22.15; N, 7.72.

9,10-Difluoroanthracene (Ib).—A mixture of 75 g of commercial steel wool (washed with CCl_4) and 55 g of 9,9,10,10-tetrafluoroanthracene[45] was heated in a shaker tube for 6 hr at 260°. The shaker tube contents were extracted with hot benzene, and the benzene was evaporated to give a dark green residual solid. The solids of two such runs were combined and passed through a chromatographic column packed with Woelm basic alumina using hexane as the eluent. There was obtained 5.0 g of 9,10-difluoroanthracene as yellow needles: mp 170–172°; infrared maxima (KBr), 6.13 (m) (C=C), 9.56 (s) (C–F), and 13.2 (s) μ (aromatic); ultraviolet absorption (EtOH), 245 mμ (ϵ 88,000), 253 (208,000), 320 (sh) (1080), 375 (2140), 352 (5250), 368 (sh) (6740), 370 (8270), 385 (435) and 391 (6200); F^{19} nmr (benzene), +3880 (singlet) cps.

Anal. Calcd for $C_{14}H_8F_2$: C, 78.50; H, 3.77; F, 17.74. Found: C, 78.18; H, 3.82; F, 18.65.

9,10-Difluoro-9,10-bis(difluoramino)-9,10-dihydroanthracene.—In an 80-ml tube containing 4.0 g (0.019 mole) of 9,10-difluoroanthracene (Ib) and 10 ml of benzene was condensed 3.0 g (0.029 mole) of N_2F_4, and the tube was sealed and heated to 35–40° for 2 hr. On evaporation of the solvent there was obtained 5.0 g of solid which was recrystallized from hexane to give as an initial crop of crystals 1.8 g (30%) of colorless needles, mp 166–167.5°, assigned as the *cis*-9,10-difluoro-9,10-bis(difluoroamino)anthracene (IIb): infrared maxima (KBr), at 10.37 (m), 10.85 (s), 11.29 (s), 11.49 (s) (NF_2), and 13.27 (s) μ (aromatic); ultraviolet absorption (ethanol), 262 (sh) mμ (ϵ 790), 267 (1040), and 274 (1120); F^{19} nmr (nitrobenzene), −5270 cps (doublet, J = ~7 cps, NF_2) and +4650 cps (triplet, J = ~7 cps, C–F).

Anal. Calcd for $C_{14}H_8F_6N_2$: C, 52.84; H, 2.53; F, 35.83; N, 8.81. Found: C, 53.23; H, 2.78; F, 34.81; N, 9.01.

On concentration of the mother liquor, there was obtained another crop of crystals which were recrystallized from petroleum ether (bp 40–60°) to give 1.7 g (28%) of white needles, mp 123–124°, assigned as the *trans*-9,10-difluoro-9,10-bis(difluoramino)-anthracene (IIIb): ultraviolet absorption (ethanol), 270 mμ (ϵ 1320), and 278 mμ (ϵ 1480); F^{19} nmr (benzene), −5310 cps (doublet, J = ~15 cps, NF_2) and +3495 cps (triplet, J = ~16 cps C–F); infrared maxima (KBr), at 10.29 (m), 10.36 (m), 10.86 (s), 11.25 (s), 11.49 (s) (NF_2), and 13.02 (s) μ (aromatic).

Anal. Calcd for $C_{14}H_8F_6N_2$: C, 52.84; H, 2.53; F, 35.83; N, 8.81. Found: C, 53.37; H, 2.70; F, 35.09; N, 9.01.

Acknowledgment.—The author wishes to acknowledge the help of the late Miller Nelson for technical assistance and of Dr. E. M. Atadan of the Explosives Department for a generous supply of N_2F_4.

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[45] W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

Chemistry of Tetrafluorohydrazine. II. Reaction with Olefins to Give N-Fluoriminonitriles[1]

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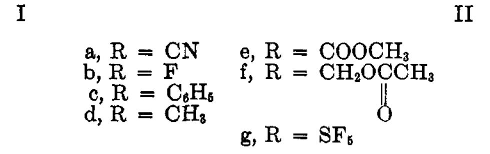
In the reaction of N_2F_4 with terminal olefins in the presence of sodium fluoride, addition of N_2F_4 to the double bond occurred first, followed by elimination of hydrogen fluoride to give N-fluoriminonitriles. *syn* and *anti* Isomerism was observed with these compounds by nmr and in the case of 1-cyano-N-fluoroformimidoyl fluoride (IIb), the two isomers were separated by gas chromatography.

The addition of N_2F_4[2] to anthracenes to give 1:1 adducts has been reported in the preceding paper[3] of this series. When the difluoramino group is attached to hydrogen-substituted carbon, there is the possibility of eliminating HF from the adducts. This suggests that the addition of N_2F_4 to an olefin could be carried out in the presence of an anhydrous base in an appropriate solvent, and that the 1:1 adduct formed initially could lose hydrogen fluoride to give in one step an N-fluorimino derivative. In this paper the synthesis and reactions of a number of novel N-fluoriminonitriles prepared by this method are described.

Reactions of the terminal olefins Ia–g with N_2F_4 were run in an autoclave containing a solvent and powdered sodium fluoride, taking the precautions outlined in the Experimental Section. The products IIa–g (obtained in 30–70% yield) were purified either by distillation or gas chromatography with precautions appropriate to the handling of potentially explosive compounds. Their structures were assigned on the basis of analytical data and infrared, mass, proton, and fluorine nmr



$$\underset{\text{I}}{CH_2{=}CHR} \xrightarrow{N_2F_4} \left[\begin{matrix} NF_2 & NF_2 \\ | & | \\ CH_2 & \!\!-\!\!CHR \end{matrix}\right] \xrightarrow[-3HF]{NaF} \underset{anti}{NC\overset{\overset{FN}{\|}}{C}R} + \underset{syn}{NC\overset{\overset{NF}{\|}}{C}R} \quad \text{II}$$

a, R = CN
b, R = F
c, R = C_6H_5
d, R = CH_3
e, R = $COOCH_3$
f, R = $CH_2OC(=O)CH_3$
g, R = SF_5

spectra. The infrared spectra of these compounds contain strong absorption peaks between 10.00 and 12.00 μ, characteristic of the N–F stretching vibration.[3] In many cases, especially when NF_2 groups are present, this absorption appears as a number of peaks,

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[1] A. L. Logothetis, U. S. Patent, 3,215,709 (1965).

[2] C. B. Colburn and A. Kennedy, *J. Am. Chem. Soc.*, **80**, 5004 (1958); C. S. Cleaver, U. S. Patent, 2,958,634 (1960).

[3] A. L. Logothetis, *J. Org. Chem.* **31**, 3686 (1966).

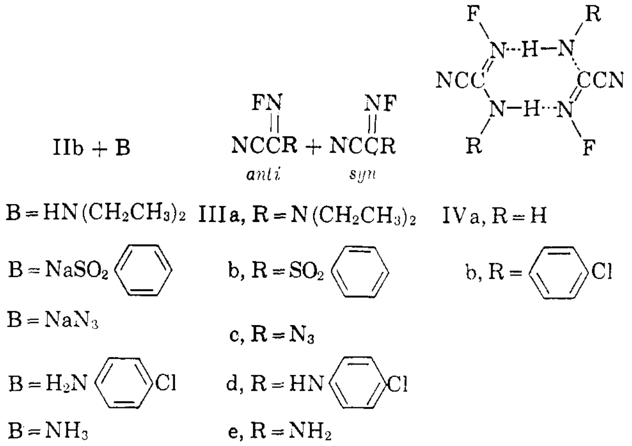
and, when =NF groups are present, it appears as only one or two strong peaks. The F^{19} nmr spectra of these compounds show the fluorine resonance of the NF_2 and =NF groups appear at lower fields from the aliphatic C–F peaks (at about −4000 to −8000 cps from $CFCl_2$-$CFCl_2$).[3]

Acrylonitrile (Ia) subjected to the above treatment gave N-fluoriminomalononitrile (IIa) as a stable liquid, bp 65–66°, with an infrared spectrum transparent in the C–H absorption region and a single peak in the fluorine nmr.

Sodium fluoride was not a strong enough base to eliminate hydrogen fluoride at temperatures below 150° when vinyl fluoride was the olefin. For this reason, the vinyl fluoride–N_2F_4 adduct was prepared initially in *o*-dichlorobenzene, and the hydrogen fluoride was eliminated by slow addition of the solution to a suspension of cesium fluoride in *o*-dichlorobenzene. The possibility of *syn* and *anti* isomers exists in all cases of the products having the structure II where R is different from a cyano group. This was verified when a gas chromatographic anaylsis of IIb indicated the presence of two isomers in 1:3 ratio. These isomers were separated by preparative gas chromatography and were assigned the *syn*- and *anti*-1-cyano-N-fluoroformidoyl fluoride (IIb) structures, respectively, on the basis of their F^{19} nmr spectra.[4] It is assumed that in the isomer where the two fluorines are *trans* to each other (*anti*-IIb), the coupling constant, J_{F-F}, will be larger than in the isomer where the two fluorines are *cis* to each other (*syn*-IIb).[5] Thus, the isomer with J_{F-F} = 265 cps is assigned the *anti*, and the isomer with J_{F-F} = 52 cps the *syn* configuration, respectively. The chemical shifts of the fluorines attached to the carbon correlate well with the above assignment,[6,7] *anti*-IIb having the C–F resonance in a higher magnetic field (shielded), +1920 cps, than the *syn*-IIb, 0 cps.

Both these isomers react with nucleophilic reagents with replacement of the fluorines attached to carbon, the N–F bond being left intact as shown by infrared and fluorine nmr spectra of the products. Thus, *syn*-IIb gave *syn*-IIIa and b (Chart I), and *anti*-IIb gave *anti*-IIIa and b when treated with diethylamine and sodium sulfinate, respectively. However, when ammonia and *p*-chloroaniline were the nucleophiles, only one isomer of IIIe and d was obtained from both *syn*- and *anti*-IIb. A molecular weight determination (boiling point elevation in benzene) of IIIe gave a value of 147 (calcd 87 for the monomer and 174 for the dimer). It appears that a dimer associated through hydrogen bonding, as depicted in IV, exists in equilibrium with the monomer. The fact that both *syn*- and *anti*-IIb gave the same IIIe and d can also be explained by the tendency of both configurational isomers to go to a thermodynamically more stable dimeric structure such as IVa and b.

CHART I



Sodium azide also reacted with 1-cyano-N-fluoroformimidoyl fluoride (mixture of *syn*- and *anti*-IIb) to give the corresponding mixture of *syn*- and *anti*-1-cyano-N-fluoroformimidoyl azide (IIIc). Attempts to isolate the pure azide led to explosions. It is stable in acetonitrile solution, however, and when treated with cyclopentene, it evolved nitrogen and yielded 1-cyano-N-cyclopentylidene-N-fluoroformimidine as a mixture of *syn* and *anti* isomers.

N-Fluoriminophenylacetonitrile (IIc) was isolated from styrene (Ic) and N_2F_4. The product was a mixture of *syn* and *anti* isomers as indicated by the two fluorine peaks in the nmr, and no attempts were made to separate the two isomers. For steric reasons (phenyl larger than cyano group), it is assumed that the *anti*-IIc is the predominant isomer.

2-N-Fluoriminopropionitrile (IId) was obtained from propylene (Id). It was also a mixture of isomers as indicated by the two fluorine and the two methyl resonances in the nmr spectra. On the assumption that the coupling constant between the methyl protons and the fluorine will be larger in the *syn*-IId (*cis* position to each other) than *anti*-IId,[8] the more abundant isomer

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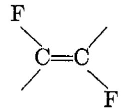
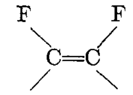
(4) The *syn* configuration is assigned to the isomer where the R group is *cis* with the fluorine on the nitrogen.

(5) The F–F coupling in fluoro olefins is around 115–125 cps when the two fluorines are *trans* to each other



and only around 39–58 cps when *cis*

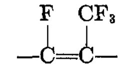


J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 335.

(6) (a) Oximes of aldehydes and unsymmetrical ketones can exist in *syn* and *anti* forms. The nmr spectra of various aldoximes were investigated by W. D. Phillips [*Ann. N. Y. Acad. Sci.*, **70**, 817 (1958)] who found that the =CH signal was in a lower magnetic field in the *syn* than in the *anti* isomer. Similarly, E. Lustig [*J. Phys. Chem.*, **65**, 491 (1961)] found that the α hydrogens in a ketoxime were also found in lower magnetic fields in the *syn* than in the *anti* isomer. (b) In 2,4-dinitrophenylhydrazones of aldehydes, the aldehydic proton *cis* to the anisotropic group is shifted to lower magnetic fields: G. J. Karabatsos, B. L. Shapiro, F. M. Vane, J. S. Fleming, and J. S. Ratka, *J. Am. Chem. Soc.*, **85**, 2784 (1963).

(7) In the case of alkyl nitrites and nitrosamines, G. J. Karabatsos and R. A. Taller [*ibid.*, **86**, 4373 (1964)] and H. W. Brown and D. P. Hollis [*J. Mol. Spectry.*, **13**, 305 (1964)] claim that α-methyl and α-methylene protons resonate at higher fields when *cis* to the nitroso oxygen, while the α-methine protons resonate at lower fields.

(8) The *cis*-coupling constants, J_{F-CH_3}, in the fluoro olefin cases, are

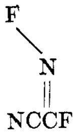
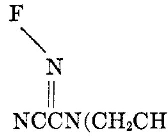
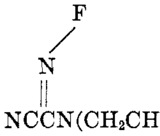
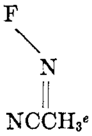
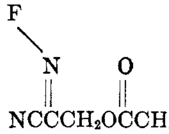
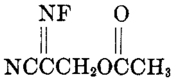


$$\overset{F}{\underset{|}{-C}}=\overset{CF_3}{\underset{|}{C-}}$$

reported to be larger than the *trans*-coupling constants [J. A. Pople, W. G. Schneider, and W. J. Bernstein "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 335, and S. Andreades, *J. Am. Chem. Soc.*, **84**, 864 (1962)], consistent with recent proposals involving direct through space coupling when the interacting fluorine atoms are close to each other [L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961)].

TABLE I

SPIN-COUPLING CONSTANTS AND CHEMICAL SHIFTS OF *syn*- AND *anti*-N-FLUORIMINO COMPOUNDS[a]

Compound	Fluorine chem shift, cps[b]	Proton chem shift, τ	Coupling constants, cps	
			J_{F-F}	J_{H-}
 *anti*-IIb	−2930 (N–F)[c] +1920 (C–F)[c]		265	
 $\mathrm{NC\overset{NF}{\overset{\|}{C}}F}$[d] *syn*-IIb	−3650 (N–F)[c] 0 [C–F)[c]		52	
 *anti*-IIIa	−1805 (N–F)[c]	6.6 (quartet, CH_2)[e] 8.8 (triplet, CH_3)[e]		
 *syn*-IIIa	−1670 (N–F)[c]	6.5 (quartet split into doublets, CH_2) 8.73 (triplet, CH_3)[e]		1.5
 *anti*-IId	−7300 (NF)[c]	0.15 (singlet)		0
 $\mathrm{NC\overset{NF}{\overset{\|}{C}}CH_3}$[f] *syn*-IId	−6588 (N–F)[c]	7.80 (doublet, CH_3)		4
 *anti*-IIf	−3740 (N–F)[c] −3740 (N–F)[c]	4.90 (doublet, CH_2) 4.90 (doublet, CH_2) 7.80 (singlet, CH_3)		3
 $\mathrm{NC\overset{NF}{\overset{\|}{C}}CH_2O\overset{O}{\overset{\|}{C}}CH_3}$[f] *syn*-IIf	−3395 (N–F)[c]	4.97 (doublet, CH_2) 7.84 (singlet, CH_3)		3.8

[a] All spectra were run neat. [b] From 1,2-difluoro-1,1,2,2-tetrachloroethane. [c] All the resonances of the fluorines attached to nitrogen are relatively broad peaks owing to the quadrupolar relaxation of the N^{14} nucleus, and spin–spin coupling with other fluorines and with protons is obscured. [d] Run at −80° for better resolution. [e] The H–H coupling in the ethyl groups is in the range of 7 cps. [f] The *syn* and *anti* isomers were not separated pure. The nmr of the mixture was taken and the resonances for each isomer were assigned following the arguments developed in the text. Ratio of *syn*-IId:*anti*-IId about 1:6 and *syn*-IIf:*anti*-IIf about 1:3.

was assigned the *syn*-IId configuration (see Table I). Similarly, 3-acetoxy-2-N-fluoriminopropionitrile (IIf), prepared from allyl acetate (If) and N_2F_4, appeared as a mixture of two isomers, the *syn*-IIf being present in larger amounts. The methyl N-fluoriminocyanoacetate (IIe) and 1-cyanofluoriminomethylsulfur pentafluoride (IIg), prepared from the corresponding methyl acrylate (Ie) and vinylsulfur pentafluoride[9] (Ig), showed only one peak in the fluorine nmr. Because of the relatively large size of the ester group in Ie and of the SF_5 group in Ig, it is assumed that only the *anti* isomers are present.

Experimental Section[10]

General Procedure.—The following reactions were carried out in 80- or 240-ml Hastelloy-C lined shaker tubes behind a barricade. *Caution is essential in handling N_2F_4.* Reactions should be carried out on as small a scale as possible to minimize laboratory handling hazards of the products. *Adequate shielding is essential* during work-up of the products as explosions may occur. For storage and handling of N_2F_4, previously fluorinated Monel or stainless steel cylinders fitted with Monel valves are recommended. Tetrafluorohydrazine is conveniently stored at −80° under 1–2 atm of pressure. All distillations of difluoroamino products were carried out behind shields, and addition of a distillation chaser, such as "Halocarbon Oil" (Halocarbon Products Corp., Series 12–21), is recommended to prevent explosions of "dry" distillation pots.

The procedure for carrying out the addition reactions was as follows. The olefin, sodium fluoride, and solvent were charged into the shaker tube, and the tube was cooled (−80°) and placed in position behind the barricade. The N_2F_4 was charged into the cold tube by pressure drop from a barricaded cylinder, and the tube was heated with shaking for the required time. The reactions were followed by the pressure drop observed. The tube was cooled to 25°, and volatile products were collected in a cooled, evacuated cylinder, and any residual liquid or solid products were separated and characterized in the usual way.

N-Fluoriminomalononitrile (IIa).—In a 240-ml tube containing 8.5 g (0.15 mole) of acrylonitrile, 30 g of *o*-dichlorobenzene, and 30 g of powdered sodium fluoride were condensed 17 g (0.163 mole) of N_2F_4. The tube was sealed, and the temperature was raised slowly to 50° (*violent explosions have occurred when the temperature was raised too fast*) and kept at this temperature for 1 hr. Then the temperature of the tube was raised slowly to 120° and held there for 3 hr. The products of three identical runs were combined, and the volatile products were distilled into a Dry Ice trap *in vacuo* and fractionated to give 29 g (66%) of N-fluoriminomalononitrile as a colorless liquid, bp 65–66°, homogeneous to gas chromatography. Infrared maxima were observed at 4.43 (s) ($C\equiv N$), 6.45 (s) ($C\equiv N$), and 10.25 (s) μ (N–F); F^{19} nmr (neat) spectra showed only one peak at −8880 cps (singlet); and the mass spectrum is given in Table II.

Anal. Calcd for C_3FN_3: F, 19.59; N, 43.32. Found: F, 19.48; N, 43.30.

TABLE II

MASS SPECTRUM

m/e	Ion	Abundance, %
26	CN^+	47.2
32	C_2N^+	45.3
45	CNF^+	72.6
52	$(CN)_2^+$	162.0
78	$(CN)_3^+$	58.1
97	$(NC)_2C{=}NF^+$	100.0

An oily mixture of 1:1 adducts was formed when equivalent amounts of N-fluoriminomalononitrile and cyclopentadiene were mixed in petroleum ether (bp 40–60°): infrared maxima,

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(9) J. R. Case, N. H. Ray, and H. L. Roberts, *J. Chem. Soc.*, 2066, 2070 (1961).

(10) All melting points were taken on a Fisher-Johns block and are not corrected. Boiling points are not corrected. Mass spectra were obtained on a Consolidated 103C instrument. Fluorine nuclear magnetic resonance spectra were obtained with a high-resolution spectrometer and associated electromagnet, both manufactured by Varian Associates operating at 56.4 Mc/sec and approximately 14,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (cps) from the F^{19} resonance of 1,2-difluoro-1,1,2,2-tetrachloroethane ("Freon-112"). One should add +3826 cps in order to get frequencies with respect to $CFCl_3$ ("Freon-11"). Negative frequency displacements are for resonances at lower field than the reference. Proton nmr spectra were determined with a Varian Associates A-60 spectrometer and are calibrated in τ values. The infrared spectra were determined with a Perkin-Elmer, Model 21, spectrophotometer. Only the peaks relative to structural arguments are recorded as weak (w), medium (m), or strong (s).

(neat) 3.28 (=CH), 3.55, 3.42, and 3.53 (CH), 4.48 (CN), and 6.06 μ (C=C); F^{19} nmr (CCl_4); single peaks at −2076 cps and −1079 cps in about 1:2 ratio indicating the possible presence of two isomers.

Anal. Calcd for $C_8H_6FN_3$: C, 58.89; H, 3.71; F, 11.66; N, 25.76. Found: C, 59.67; H, 3.98; F, 11.80; N, 25.91.

1-Cyano-N-fluoroformimidoyl Fluoride (IIb).—In a 240-ml tube containing 25 g of *o*-dichlorobenzene were condensed 9.0 g (0.195 mole) of vinyl fluoride and 16 g (0.154 mole) of N_2F_4, and the tube was sealed and heated to 103° for 1 hr. The products from three such reactions were combined and were added dropwise into a well-stirred mixture of 50 g of cesium fluoride in 150 ml of *o*-dichlorobenzene causing an exothermic reaction with evolution of gases. After the addition was complete, the mixture was heated to 80° for 2 hr. The volatile products (14.5 g, 35%) were collected in a Dry Ice trap. Gas chromatographic analysis on a 12-ft column packed with 20% "Kel-F" ester on 40–60 mesh firebrick at 0° and helium flow of 60 ml/min showed that a mixture of two components in a 1:3 ratio in order of elution was mainly present. They were separated by preparative gas chromatography. The component that eluted first (retention time 9.2 min) was assigned as the *anti*-1-cyano-N-fluoroformimidoyl fluoride; infrared spectrum (gas) maxima were observed at 4.41 (w) (CN), 6.03 (m), and 6.08 (m) (C=N), 7.65 (s) and 7.74 (s) (C–F), and 10.13 (s), 10.17 (s), and 10.26 (s) μ (NF). The boiling point was estimated as −3 ± 0.5° and the heat of vaporization, ΔH_{vap} as 6350 cal/mole from the vapor pressure equation, $\log P_{mm} = -1390/T + 8.01$. The main peaks of the mass spectrum are given in Table III. The component that eluted next (retention time 11.0 min) was assigned as the *syn*-1-cyano-N-fluoroformimidoyl fluoride; infrared spectrum (gas) maxima were observed at 4.44 (CN), 6.10 (m) and 6.13 (m) (C=N), 7.49 (s) and 7.55 (s) (CF), and 9.94 (s), 9.98 (s), and 10.05 (s) μ (NF). The boiling point was estimated as +2 ± 0.5° and the heat of vaporization, ΔH_{vap} as 6580 cal/mole, from the vapor pressure equation, $\log P_{mm} = -1440/T + 9.13$. The main peaks of the mass spectrum are given in Table IV.

TABLE III

MASS SPECTRUM

m/e	Ion	Abundance, %
26	CN^+	28
31	CF^+	77
45	CNF^+	100
52	$(NC)_2^+$	20
57	$NCCF^+$	11
71	$NCC{=}NF^+$	35
90	$NC\underset{\mathrm{F}}{\underset{\vert}{C}}{=}NF^+$	92

TABLE IV

MASS SPECTRUM

m/e	Ion	Abundance, %
26	CN^+	20
31	CF^+	77
45	NCF^+	100
52	$(NC)_2^+$	10
57	$NCCF^+$	9
71	$NCC{=}NF^+$	44
90	$NC\underset{\mathrm{F}}{\underset{\vert}{C}}{=}NF^+$	87

Reactions of 1-Cyano-N-fluoroformimidoyl Fluoride (IIb). A. With Diethylamine.—A mixture of 25 ml of ethyl ether and 5 ml of diethylamine was cooled to −78°, and 1.2 g of *syn*-1-cyano-N-fluoroformimidoyl fluoride was condensed into the mixture causing an exothermic reaction. The mixture was allowed to come to room temperature, the amine hydrofluoride was removed by filtration, and the filtrate was distilled to give 1.6 g of *syn*-1-cyano-N,N-diethyl-N′-fluoroformamidine (IIIa) as a colorless liquid, bp 80° (4 mm), $n^{25}D$ 1.4502. Infrared maxima (neat) were observed at 4.50 (w) (CN), 6.20 (s) (C=N), and 11.15 (s) μ (NF), and ultraviolet absorption (ethanol) at 252 mμ (ε 5100).

Anal. Calcd for $C_6H_{10}FN_3$: C, 50.33; H, 7.04; F, 13.28; N, 29.36. Found: C, 50.51; H, 7.84; F, 12.94; N, 29.82.

Using exactly the same procedure as above for the *anti* isomer, there was obtained the *anti*-1-cyano-N,N′-diethyl-N-fluoroformamidine (IIIa) as a colorless liquid, bp 70° (2 mm), with infrared maxima (neat) at 4.45 (w) (CN), 6.40 (s) (C=N), and 11.6 (s) μ (NF), and ultraviolet absorption (ethanol) at 272 mμ (ε 3300).

Anal. Calcd for $C_6H_{10}FN_3$: C, 50.33; H, 7.04; F, 13.28; N, 29.36. Found: C, 50.78; H, 7.80; F, 12.84; N, 29.66.

B. **With Ammonia.**—The same procedure as above was followed using the *anti*-1-cyano-N-fluoroformimidoyl fluoride (IIb) and ammonia. The excess ammonia was allowed to evaporate, the ammonium fluoride was removed by filtration, and the solvent removed *in vacuo* to give a solid residue. The solid was recrystallized from benzene–hexane to give 1-cyano-N′-fluoroamidine (IIIe) as slightly yellow needles, mp 107–108°. Infrared maxima (KBr) were observed at 2.92 (s), 3.12 (s) (NH_2), 4.38 (w) (CN), 6.06 (s) (C=N), 6.16 (s) (NH_2), 11.07 (s) and 11.40 (s) μ (NF); ultraviolet absorption at 224 mμ (ε 5400); F^{19} nmr ($CDCl_3$), −2075 cps (singlet, N–F); proton nmr ($CDCl_3$), τ 2.8 (br, NH_2).

Anal. Calcd for $C_2H_2FN_3$: C, 27.61; H, 2.32; F, 21.84; N, 48.30. Found: C, 28.60; H, 2.64; F, 21.55; N, 47.89.

When the *syn* isomer was used the same 1-cyano-N′-fluoroformamidine (IIIe) was obtained identical in all respects with the above sample.

C. **With *p*-Chloroaniline.**—A solution of 2.0 g of *p*-chloroaniline in 15 ml of ethyl ether was cooled to −78°, and 0.6 g of *anti*-1-cyano-N-fluoroformimidoyl fluoride (IIb) was condensed into the solution. The mixture was allowed to come to room temperature, the *p*-chloroaniline hydrofluoride was removed by filtration, and the ether was removed *in vacuo* to leave a solid. The solid was recrystallized from hexane to give 1.2 g (90%) of N-*p*-chlorophenyl-1-cyano-N′-fluoroformamidine (IIId), mp 106–108°. Infrared maxima (KBr) were observed at 3.08 (s), 3.23 (w) (NH), 3.27 (w) (=CH), 4.44 (w) (CN), 6.16 (s) (C=N), 11.0 (s), 11.92 (s) μ (NF), 12.63 (s), and 13.85 (m) μ (*p*-substituted phenyl); ultraviolet absorption (ethanol) at 230 mμ (sh) (ε, 8350) and 272 mμ (8060); F^{19} nmr ($CDCl_3$), −2810 cps (singlet, N–F); and proton nmr ($CDCl_3$), a quadruplet at τ 1.7 (aromatic protons), the NH band being too broad to be detected.

Anal. Calcd for $C_8H_5ClFN_3$: C, 48.63; H, 2.55; Cl, 17.94; F, 9.62; N, 21.27. Found: C, 49.32; H, 2.72; Cl, 18.14; F, 9.59; N, 21.10.

When *syn*-IIb was used, the same N-*p*-chlorophenyl-1-cyano-N′-fluoroformamidine (IIId) was obtained, identical in all respects with the above sample.

D. **With Sodium Phenylsulfinate.**—A flask containing 0.55 g of sodium phenylsulfinate and 5 ml of acetonitrile was cooled to −78°, and 0.3 g of *syn*-1-cyano-N-fluoroformimidoyl fluoride was condensed into it. The mixture was allowed to come to room temperature, the sodium fluoride was removed by filtration, and the solvent was evaporated to leave *syn*-α-(fluorimino)-phenylsulfonylacetonitrile (IIIb) as a white solid which was recrystallized from petroleum ether (bp 40–60°), mp 65–66°. Infrared maxima (KBr) were observed at 3.25 (m) (=CH), 4.47 (w) (CN), 6.19 (m) (C=N), 7.32 (s) and 8.68 (s) (SO_2), and 10.54 (s) and 10.64 (s) μ (NF); ultraviolet absorption (ethanol) at 217 mμ (ε, ~8050), 245 (~4200), and 275 (sh), (~2600).

Anal. Calcd for $C_8H_5FN_2O_2S$: C, 45.28; H, 2.38; N, 13.21. Found: C, 45.49; H, 2.47; N, 13.30.

When the *anti* isomer was used as the starting material, *anti*-α-(fluorimino)phenylsulfonylacetonitrile (IIIb) was formed, mp 61–62°. Infrared maxima (KBr) were observed at 3.30 (m) (=CN), 4.45 (w) (CN), 6.30 (m) (C=N), 7.30 (s), 8.42 (s), 8.57 (s) (SO_2), and 11.0 (s) μ (NF); ultraviolet absorption at 222 mμ (ε 7060), 256 (4030), 270 mμ (sh) (3000), and 277 mμ (sh) (2482).

Anal. Calcd for $C_8H_5FN_2O_2S$: F, 8.95; N, 13.21. Found: F, 8.92; N, 13.02.

E. **With Sodium Azide.**—A suspension of 0.41 g (6.3 mmoles) of sodium azide and 5 ml of acetonitrile was cooled to −78°, and 0.60 g (6.7 mmoles) of a mixture of *syn*- and *anti*-1-cyano-N-fluoroformimidoyl fluoride was condensed into the suspension. The mixture was allowed to come to room temperature, and the infrared spectrum of the supernatant solution showed peaks at 4.65 (s) (N_3), 6.35 (s) (C=N), 10.30 (s) and 10.70 (s) μ (NF), indicating that the intermediate azide IIIc had been formed. The mixture was treated with 2.0 ml of cyclopentene diluted with ethyl ether causing evolution of nitrogen. The sodium fluoride was removed by filtration, the solvent evaporated *in vacuo*, and the residue was distilled, bp ~50° (0.1 mm), to give 1-cyano-N-cyclopentylidene-N′-fluoroformimidine as an unstable liquid. Infrared maxima (neat) were observed at 4.45 (w) (CN), 5.94 (s), 6.38 (w) (C=N), and 10.85 (s) μ (NF); ultraviolet absorption (ethanol) at 270 mμ (sh), (ε 1250); F^{19} nmr (CCl_4), −4580 cps (singlet), −4405 cps (singlet) for the *syn* and *anti* isomers, and proton nmr (CCl_4), at τ 7.6 (multiplet, CH_2) and 8.05 (multiplet, CH_2) in 1:1 ratio.

Anal. Calcd for $C_7H_8FN_3$: C, 54.89; H, 5.27; F, 12.41; N, 27.44. Found: C, 55.57; H, 5.53; F, 12.38; N, 27.32.

α-(Fluorimino)phenylacetonitrile (IIc).—In an 80-ml tube containing 6.0 g (0.048 mole) of styrene, 12.5 g of acetonitrile, and 12 g of powdered sodum fluoride was condensed 6.3 g (0.061 mole) of N_2F_4. The tube was sealed and heated at 125° for 3 hr. The solids were removed by filtration, and the liquid was distilled to give 4.8 g (56%) of α-(fluorimino)phenylacetonitrile as a colorless liquid, bp 40° (0.2 mm), n^{25}D 1.5280. Infrared maxima (neat), were observed at 4.48 (m) (CN), 6.26 (m), 6.43 (m), 6.7 (m) (unsaturation), 11.1 (s) μ (br, NF); ultraviolet absorption at 217 mμ (ε 6500) and 268 mμ (ε 8200); and F^{19} nmr (neat), single peaks at −6754 cps and −6012 cps in about 3.5:1 ratio (NF).

Anal. Calcd for $C_8H_5FN_2$: C, 64.72; H, 3.42; F, 12.84; N, 18.93. Found: C, 64.70; H, 3.47; F, 13.58; H, 19.04.

2-N-Fluoriminopropionitrile (IId).—In an 80-ml tube containing 25 g of *o*-dichlorobenzene and 50 g of cesium fluoride were condensed 4.5 g (0.1 mole) of propylene and 10 g (0.1 mole) of N_2F_4. The tube was sealed and heated first at 50° for 1 hr and then at 100° for 2 hr. The volatile products were collected in a Dry Ice trap *in vacuo* and were then subjected to fractionation to give 1.0 g of 2-N-fluoriminopropionitrile as a colorless liquid, bp 60° (200 mm). Infrared maxima (neat) were observed at 3.4 (w) (CH_3) 4.43 (m) (CN), 6.2 (m) (C=N), and 11.0 (s) μ (NF).

Anal. Calcd for $C_3H_3FN_2$: F, 22.07; N, 32.56. Found: 21.97; N, 32.02.

Methyl N-Fluoriminocyanoacetate (IIe).—In an 80-ml tube containing 6.0 g (0.07 mole) of methyl acrylate, 12 g of acetonitrile, and 12 g of sodium fluoride powder was condensed 7.3 g (0.07 mole) of N_2F_4. The tube was sealed and heated to 71° for 1 hr and at 125° for 2 hr. The solids were removed by filtration, and the liquids were distilled to give 3.0 g of methyl N-fluoriminocyanoacetate as a colorless liquid, bp 67–68° (25 mm), n^{25}D 1.4075. Infrared maxima (neat) were observed at 4.44 (m) (CN), 5.73 (s) [(=O)CO)], 6.3 (s) (C=N), and 10.2 (s), 10.58 (s), and 10.94 (s) μ (NF); F^{19} nmr (neat) single peak at −7766 cps (NF); and proton nmr (neat) 5.92 cps (single, CH_3).

Anal. Calcd for $C_4H_3F_4N_2$: F, 14.61; N, 21.54. Found: F, 14.56; N, 21.64.

2-Cyano-2-(fluorimino)ethyl Acetate (IIf).—In a 240-ml tube containing 6.0 g (0.06 mole) of allyl acetate, 16 g of sodium fluoride powder, and 20 g of acetonitrile was condensed 8.0 g (0.08 mole) of N_2F_4. The tube was sealed and heated to 70° for 1 hr and then to 130° for 3 hr. The solids were removed by filtration, and the liquids were distilled to give 5.0 g (58%) of 2-cyano-2-(fluorimino)ethyl acetate as a colorless liquid, bp 47° (2 mm), n^{25}D 1.4100. Infrared maxima (neat) were observed at 4.44 (w) (CN), 5.73 (s) [(=O)CO], 6.24 (w) (C=N), and 10.9 (s) μ (NF).

Anal. Calcd for $C_5H_5FN_2O_2$: N, 19.45. Found: N, 19.35.

Cyano(fluorimino)methylsulfur Pentafluoride (IIg). —In an 80-ml tube containing 7.5 g of vinylsulfur pentafluoride[9,11] 15 g of *o*-dichlorobenzene, and 10 g of sodium fluoride powder was condensed 6.0 g of N_2F_4. The tube was sealed and heated to 130° for 3 hr. The volatiles were distilled into a Dry Ice trap *in vacuo* and then fractionated to give 1.5 g of cyano(fluorimino)methylsulfur pentafluoride as a colorless liquid, bp 51°. Infrared maxima (neat) were observed at 4.44 (m) (CN), 6.3 (w) (C=N), and 10–12 (s) μ (br, SF_5, NF), and F^{19} nmr (neat) multiple peaks at −7295 cps (SF_5)[12] with a single broad peak at −7500 cps (NF). The main peaks of the mass spectrum are given in Table V.

Anal. Calcd for $C_2F_6N_2S$: F, 57.55; N, 14.14; S, 16.18. Found: F, 56.72; N, 13.40; S, 15.91.

TABLE V

MASS SPECTRUM

m/e	Ion	Abundance, %
26	CN^+	3.5
31	CF^+	8.8
32	S^+	3.1
51	SF^+	3.6
52	$(NC)_2^+$	13.1
70	SF_2^+	6.2
71	$NCC{=}NF^+$	30.0
89	SF_3^+	18.8
108	SF_4^+	3.8
127	SF_5^+	100.0

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