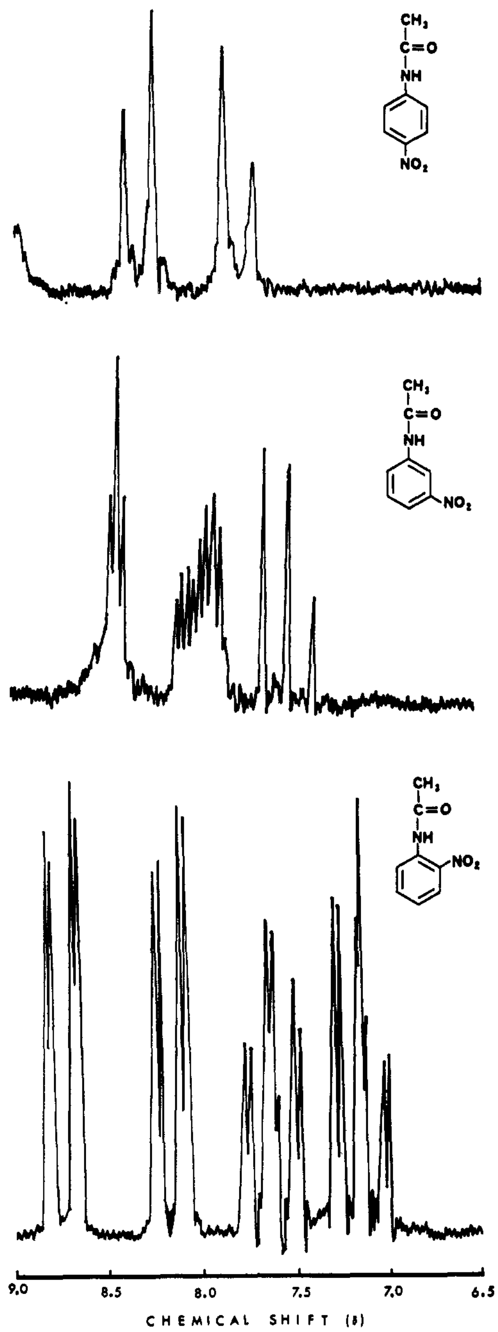

Figure 4.

able with their predicted splitting patterns. The spectra of *m*- and *p*-nitroacetanilide in the same region are also pictured for comparison. Comparing the spectra of the *o*-, *m*-, and *p*-nitroacetanilides, it can be seen that H_a in the *ortho* compound is the most deshielded aromatic proton not only in that molecule but in any compound of the series. This phenomenon has been observed for other substituents in monosubstituted acylamines.

One other interesting aspect of this study came to light when an attempt was made to extend the "*ortho* effect" to substituted phenolic esters (Figure 5). Surprisingly, there was no comparable deshielding of the H_α proton. An analysis of this unexpected result, however, now provides additional support for the original hypotheses. When scale molecular models of the acylanilines and the phenolic esters were constructed, the former were able to assume the postulated conformation. With the phenolic esters, however, the slight change in the C_{aryl}–O–C_{acyl} bond angle prevented a similar conformer from existing. The magnetic anisotropy of the carbonyl group, therefore, is no longer an important deshielding factor. Although other atoms can probably replace the nitrogen atom in compounds exhibiting the "*ortho* effect," the oxygen analogs cannot.

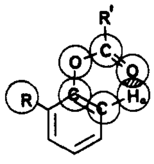

Figure 5.

In summary, *ortho*-substituted acylanilines exhibit enhanced deshielding for the proton *ortho* to the acylamine group. The effect is a combination of the steric and electronic influence of the group *ortho* to the acylamine substituent. The bulk of the group forces the acyl carbonyl oxygen into close proximity to the *ortho* hydrogen and the electronic effect produces additional deshielding acting through the aromatic ring.

Experimental Section

The nmr spectra were obtained on a Varian Associates A-60A spectrometer operating at a frequency of 60 MHz. Samples were prepared as 10% by weight solutions in either deuterated chloroform or, in the case of difficultly soluble material, deuterated dimethyl sulfoxide. Tetramethylsilane was incorporated in the solvents as an internal standard. Normal probe temperature was 35°. The compounds investigated were obtained either from commercial sources or by synthesis. Their purity was verified by the absence of extraneous peaks in the spectra.

Registry No.—Table I: I, 103-84-4; II, 351-83-7; III, 2415-85-2; IV, 122-82-7; V, 10147-71-4; VI, 104-04-1; VII, 120-66-1; VIII, 614-83-5; IX, 399-31-5; X, 614-80-2; XI, 552-32-9; XII, 881-50-5; XIII, 89-52-1; XIV, 10147-70-3; XV, 17223-64-2; XVI, 2621-70-7; XVII, 17223-66-4; XVIII, 17223-67-5.

Fluorocarbon Difluoramines and Nitriles

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The resurgence of interest in the synthesis and reactions of nitrogen–fluorine compounds is illustrated by the fact that six review articles describing various aspects of this field have been published in the last five years.[1] In general, the most suitable methods for the synthesis of nitrogen–fluorine substituted perfluoroalkyl derivatives include fluorination of nitrogen-con-

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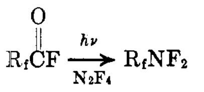
(1) (a) J. K. Ruff, *Chem. Rev.*, **67**, 665 (1967); (b) C. B. Colburn, *Chem. Brit.*, **2**, 336 (1966); (c) C. B. Colburn, *Endeavour*, **24**, 138 (1965); (d) C. B. Colburn, *Advan. Fluorine Chem.*, **3**, 92 (1963); (e) A. V. Pankratov, *Usp. Khim.*, **32**, 336 (1963); (f) C. J. Hoffman and R. G. Neville, *Chem. Rev.*, **62**, 1 (1962).

taining substrates with elemental fluorine with concomitant difficulties in controlling the reaction,[2] electrochemical fluorination, and pyrolysis of R_fSF_5 and R_f-SF_4R_f derivatives in the presence of tetrafluorohydrazine.[3]

In our search for a convenient preparation of perfluoroalkyldifluoramines which did not involve the use of elemental fluorine, we considered perfluorocarboxylic acids, -acyl chlorides, and -acyl fluorides as commercially available starting materials. We have found that photolysis[4] of the corresponding perfluoroacyl fluorides in the presence of excess tetrafluorohydrazine is a convenient and useful technique for the formation of perfluoroalkyldifluoramines.

Results and Discussion

Photolysis of perfluoroacyl fluorides in the presence of tetrafluorohydrazine (eq 1) was found to proceed smoothly and afforded the corresponding perfluoroalkyldifluoramines in high yields. The technique requires conventional quartz apparatus and ultraviolet sources and is readily adaptable to the preparation of multigram quantities of perhaloalkyldifluoramines. In general, the by-products of the reaction are those resulting from photodegradation of the excess N_2F_4 and are quite low boiling and readily separable from the desired product by vacuum-line fractionation. Vapor phase chromatography was used to follow the reactions and in all cases showed little evidence for by-product formation caused by coupling or photodegradation of the perhaloalkyl species.

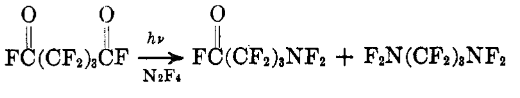


$$R_fC(=O)F \xrightarrow[N_2F_4]{h\nu} R_fNF_2 \qquad (1)$$

R_f = fluoroaliphatic radical

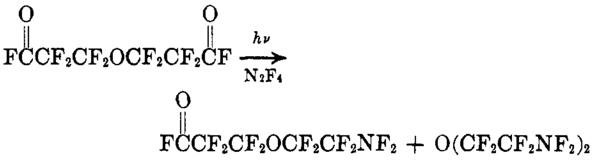
The acyl fluoride–tetrafluorohydrazine technique was also extended to difunctional materials as a general route to α,ω-bisdifluoramines.

With perfluorodiacyl fluorides, a two-step radical-radical combination reaction, occurred and resulted in the formation of the mono- and bisdifluoramino derivatives in varying yields depending primarily upon photolysis time, light intensity, and the relative proportions of starting materials. Photolysis of perfluoroglutaryl fluoride (eq 2) in the presence of a threefold excess of tetrafluorohydrazine with a 140-W source resulted in a 2:1 mixture of $F_2N(CF_2)_3CFO$ and $F_2N(CF_2)_3NF_2$. A 5 *M* excess of tetrafluorohydrazine and a 450-W ultraviolet source afforded a 5:1 ratio of the same products. In both reactions, vapor phase chromatographic analysis of the product mixtures showed the reactions to be relatively free of by-products. Although they oxidized potassium iodide, dicyclopentadienyliron, and triphenylphosphine, the perhaloalkyldifluoramines prepared in this work exhibited excellent storage stability. For example, a liquid sample of $F_2N(CF_2)_3CFO$ was stored in a glass bulb at room temperature for over one year without significant decomposition.



$$FC(=O)(CF_2)_3C(=O)F \xrightarrow[N_2F_4]{h\nu} FC(=O)(CF_2)_3NF_2 + F_2N(CF_2)_3NF_2 \qquad (2)$$

The generality of the procedure was further demonstrated by the preparation of $F_2NCF_2CF_2OCF_2CF_2CFO$ and $O(CF_2CF_2NF_2)_2$ from perfluorooxydipropionyl fluoride[5] (eq 3). Irradiation of a 3:1 mixture of N_2F_4 and $O(CF_2CF_2CFO)_2$, which was followed by addition of 3 molar equiv of N_2F_4 and continued irradiation, afforded a 2:1:1 product mixture of the corresponding mono- and bisdifluoramino derivatives and unreacted starting material, respectively.



$$FC(=O)CF_2CF_2OCF_2CF_2C(=O)F \xrightarrow[N_2F_4]{h\nu} FC(=O)CF_2CF_2OCF_2CF_2NF_2 + O(CF_2CF_2NF_2)_2 \qquad (3)$$

In another run taken to completion, irradiation of a 4:1 molar ratio of tetrafluorohydrazine (two increments) and perfluorooxydipropionyl fluoride afforded a 65% isolated yield of $O(CF_2CF_2NF_2)_2$ after preparative vapor phase chromatographic purification.

Since it has been demonstrated that perhaloalkyldifluoramines were readily prepared *via* the photolytic reaction of acyl fluorides and tetrafluorohydrazine, it was of interest to extend our earlier studies on dicyclopentadienyliron reductive defluorination, which afforded the fluorimines, $-CF{=}NF$,[6] to a synthesis technique for the preparation of nitriles. Firth and coworkers have reported the complete defluorination of tetrafluorohydrazine with triphenylphosphine.[7] We have found that triphenylphosphine reacts smoothly with $-CF_2NF_2$ derivatives (eq 4) in a 2:1 stoichiometry to afford the corresponding nitriles in 80–90% yields. The reaction is rapid, free of by-products, other than the difluorophosphorane, and affords essentially pure nitrile after vacuum-line fractionation if a 10–20% excess of triphenylphosphine is used. Since the difluorophosphorane by-product precipitates rapidly from the reaction mixture below room temperature, separation of higher boiling nitriles is a relatively simple procedure.

$$R_fCF_2NF_2 + 2(C_6H_5)_3P \xrightarrow[C_6H_6]{25^\circ} R_fC{\equiv}N + 2(C_6H_5)_3PF_2\downarrow \qquad (4)$$

$$R_f = CF_3,\ CFCl_2$$

Another use of triphenylphosphine as a defluorinating agent was demonstrated in the preparation of a dinitrile from the corresponding α,ω-bisdifluoramine (eq 5). Thus, reaction of triphenylphosphine with

$$O(CF_2CF_2NF_2)_2 + 4(C_6H_5)_3P \longrightarrow O(CF_2CN)_2 + 4(C_6H_5)_3PF_2\downarrow \qquad (5)$$

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[2] An exception to the usual degradation during fluorination of nitrogen-containing substrates with elemental fluorine is the low temperature catalytic fluorination procedure reported recently: J. K. Ruff, *J. Org. Chem.*, **32**, 1675 (1967).

[3] R. K. Pearson and R. D. Dresdner, *J. Amer. Chem. Soc.*, **84**, 4743 (1962).

[4] J. F. Harris, Jr., *J. Org. Chem.*, **30**, 2182 (1965).

[5] V. Ya. Kazakov, R. A. Dzerzhinskaya, V. I. Tsimbalist, and E. A. Shishkin, *Zh. Obshch. Khim.*, **36**, 1807 (1966).

[6] R. A. Mitsch, *J. Amer. Chem. Soc.*, **87**, 328 (1965).

[7] W. C. Firth, S. Frank, M. Garber, and V. P. Wystrach, *Inorg. Chem.*, **4**, 765 (1965).

TABLE I

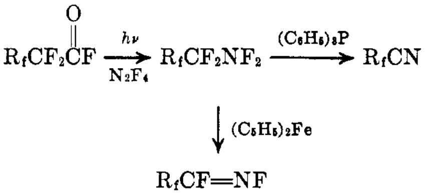
^{19}F NUCLEAR MAGNETIC RESONANCE SPECTRA

Formula	Registry no.	Group	ϕ*	Group	ϕ*
$CF_3\overset{a}{CF_2}\overset{b}{CF_2}NF_2$	423-32-5	CF_3	82.3	CF_2 (b)	117.0
		CF_2 (a)	127.6	NF_2	−17.0
$F\overset{O}{\overset{\|}{C}}\overset{a}{CF_2}\overset{b}{CF_2}\overset{c}{CF_2}NF_2$[a]	17223-69-7	$F\overset{O}{\overset{\|}{C}}$—	−21.8	CF_2 (c)	117.7
		CF_2 (a)	120.4	NF_2	−14.7
		CF_2 (b)	125.2		
$\overset{a}{CF_2}(\overset{b}{CF_2}NF_2)_2$[a]	376-74-9	CF_2 (a)	127.2	NF_2	−13.8
		CF_2 (b)	119.2		
$F\overset{O}{\overset{\|}{C}}\overset{a}{CF_2}\overset{b}{CF_2}O\overset{c}{CF_2}\overset{d}{CF_2}NF_2$	17223-71-1	$F\overset{O}{\overset{\|}{C}}$	−23.4	CF_2 (c)	83.0
		CF_2 (a)	122.0	CF_2 (d)	119.5
		CF_2 (b)	85.5	NF_2	−16.9
$O(\overset{a}{CF_2}\overset{b}{CF_2}NF_2)_2$	17223-72-2	CF_2 (a)	83.2	NF_2	−16.9
		CF_2 (b)	119.6		
$O(CF_2CN)_2$	17223-73-3	CF_2	58.6		

[a] External reference $CFCl_3$.

$O(CF_2CF_2NF_2)_2$ in benzene afforded the desired dinitrile in 90% yield.

Contrary to normal amide dehydration techniques, the reaction sequence (eq 6) involving acyl fluoride to



$$R_fCF_2\overset{O}{\overset{\|}{C}}F \xrightarrow[N_2F_4]{h\nu} R_fCF_2NF_2 \xrightarrow{(C_6H_5)_3P} R_fCN \qquad (6)$$

$$R_fCF_2NF_2 \xrightarrow{(C_5H_5)_2Fe} R_fCF{=}NF$$

difluoramine to nitrile represents a convenient approach to the preparation of perhalonitriles having one carbon atom less than the starting acid fluoride. On the other hand, when the difluoramine synthesis is coupled with dicyclopentadienyliron reduction[6] the corresponding fluorimines are prepared readily from commercially available fluorocarbon intermediates.

Experimental Section

Preparation of $C_3F_7NF_2$.—A gaseous mixture of 1.75 g (8.1 × 10^{-3} mol) of $CF_3CF_2CF_2CFO$ and 0.416 g (4.05 × 10^{-3} mol) of N_2F_4 in a 300-cc quartz bulb was irradiated for 20 hr with a Hanovia 140-W ultraviolet lamp. The temperature of the reactor was about 40°. The principal product, isolated in greater than 90% yield by preparative scale gas chromatography, was identified as $CF_3CF_2CF_2NF_2$ by infrared, mass, and ^{19}F nmr spectral comparisons with an authentic sample.[2]

Preparation of $F_2N(CF_2)_3CFO$ and $F_2N(CF_2)_3NF_2$.—A mixture of 0.59 g (2.41 × 10^{-3} mol) of $OFC(CF_2)_3CFO$ and 0.752 g (7.23 × 10^{-3} mol) of N_2F_4 in a 300-cc quartz bulb was irradiated with a 140-W Hanovia ultraviolet lamp. After 6.5 hr of irradiation, vpc analysis of the mixture showed that all of the N_2F_4 had been consumed with approximately 30% of the perfluoroglutaryl fluoride unreacted. The molar ratio of $F_2N(CF_2)_3CFO$ and $F_2N(CF_2)_3NF_2$ was about 2:1. Conversion into the two products was clean. Preparative vapor phase chromatography on a 12 ft × 0.25 in. KF 8126[8] column operating at 25° afforded the purified products.

The monodifluoroamino derivative, $F_2N(CF_2)_3CFO$, was identified by infrared and ^{19}F nmr spectroscopy (Table I) and elemental analysis. The infrared spectrum showed absorptions at 5.3 (C=O), 7.8–8.8 (CF), and 10.5–11.8 μ (NF).

Anal. Calcd for C_4F_9NO: C, 19.3; F, 68.7. Found: C, 19.0; F, 68.2.

1,3-Bis(difluoramino)perfluoropropane was identified by infrared and ^{19}F nmr spectral comparisons with authentic samples.[8,9]

Preparation of $F_2N(CF_2)_2O(CF_2)_2CFO$ and $O(CF_2CF_2NF_2)_2$.—A mixture of 1.22 g (3.94 × 10^{-3} mol) of $O(CF_2CF_2CFO)_2$ and 1.23 g (11.8 × 10^{-3} mol) of N_2F_4 in a 300-cc quartz bulb was irradiated with a 140-W Hanovia ultraviolet lamp. Monitoring of the reaction by vpc showed that after about 5 hr all of the N_2F_4 was consumed, but more than 50% of the $O(CF_2CF_2CFO)_2$ remained. The volatile by-products were removed by a vacuum-line distillation and 12.0 × 10^{-3} mol of N_2F_4 was added to the reactor. Irradiation was resumed for an additional 5 hr. Vapor phase chromatographic analysis of the final reaction mixture showed $F_2NCF_2CF_2OCF_2CF_2CFO$, $O(CF_2CF_2NF_2)$, and $O(CF_2CF_2CFO)_2$ in a molar ratio of 2:1:1, respectively. Isolation of pure fractions of these compounds was accomplished by vpc.

The monodifluoramino derivative, $F_2NCF_2CF_2OCF_2CF_2CFO$, was identified by infrared, mass, and ^{19}F nmr spectroscopy (Table I) and elemental analysis. Infrared absorptions appeared at 5.3 (C=O), 7.8–8.9 (CO and CF), and 9.9–10.6 μ (NF).

Anal. Calcd for $C_5F_{11}NO_2$: F, 66.3; N, 4.5; mol wt, 315. Found: F, 63.8; N, 4.3; mol wt, 304 (effusion, mass spectrometer).

The bisdifluoramino derivative, $O(CF_2CF_2NF_2)_2$, bp 66°, was identified by infrared, mass, and ^{19}F nmr spectroscopy (Table I) and elemental analysis. Principal bands in the infrared spectrum appeared at 7.9–8.6 (CO and CF) and 10.1–10.6 μ (NF).

Anal. Calcd for $C_4F_{12}N_2O$: F, 71.0; N, 8.8; mol wt, 320. Found: F, 70.0; N, 8.6; mol wt, 320 (effusion, mass spectrometer).

In another run taken to completion by irradiating a mixture of 3.1 g (10.0 × 10^{-3} mol) of perfluorooxydipropionyl fluoride and 3.96 g (38.0 × 10^{-3} mol) of tetrafluorohydrazine, in two equal increments, afforded 2.08 g (65%) of $O(CF_2CF_2NF_2)_2$ after purification by preparative vapor phase chromatography.

Preparation of CF_3CN.—A 0.262-g (1 × 10^{-3} mol) sample of triphenylphosphine and 3 ml of benzene were added to a 15-cc glass reactor. To the reactor, which had been cooled to −196°, was added 0.085 g (5 × 10^{-4} mol) of 1-difluoraminoperfluoroethane (Hynes Chemical Corp.) by condensation. The mixture was allowed to warm to room temperature; a colorless precipitate [$(C_6H_5)_3PF_2$] formed immediately. Fractionation through −78° and −196° receivers afforded 3.9 × 10^{-4} mol (78%) of pure trifluoroacetonitrile. Identification was by spectral comparisons with published data.

Preparation of $CFCl_2CN$.—Following the above procedure, 0.262 g (1 × 10^{-3} mol) of triphenylphosphine in 2 ml of benzene

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(8) A chlorotrifluoroethylene tetramer oil.

(9) F. P. Avonda, J. A. Gervasi, and L. A. Bigelow, *J. Amer. Chem. Soc.*, **78**, 2798 (1956).

was allowed to react with 0.102 g (5×10^{-4} mol) of 1,1-dichloro-2-difluoraminoperfluoroethane for 1 hr. Fractionation through −55 and −196° traps gave 4.5×10^{-4} mol (90%) of pure dichlorofluoroacetonitrile in the −196° receiver. Identification was by spectral comparisons with an authentic sample.

Preparation of $NCCF_2OCF_2CN$.—A solution of triphenylphosphine (2.5 g, 9.6×10^{-3} mol) and $O(CF_2CF_2NF_2)_2$ (0.6 g, 1.9×10^{-3} mol) in 10 cc of benzene was warmed slowly from −196° to room temperature. After reaching room temperature, the reaction mixture was stirred about 2 hr. Gas chromatographic analysis showed only a trace of unreacted $O(CF_2CF_2NF_2)_2$. The desired product, 0.28 g (90%), bp 35°, was isolated by passage through a −78° trap to remove benzene, followed by vapor phase chromatography, and identified by infrared, mass, and ^{19}F nmr (Table I) spectroscopy and elemental analysis. The infrared spectrum showed absorptions at 4.4 (CN) and 7.8–9.0 μ (CO and CF).

Anal. Calcd for $C_4F_4N_2O$: F, 45.2; N, 16.6; mol wt, 168. Found: F, 44.6; N, 16.3; mol wt, 165 (gas density).

Registry No.—CF_3CN, 353-85-5; $CFCl_2CN$, 353-82-2.

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