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The Action of Elementary Fluorine upon Organic Compounds. XXVII. The Direct Fluorination of Fluorinated Aliphatic Dinitriles[1]

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This paper describes the direct jet fluorination of the dinitriles of perfluorinated malonic, succinic and glutaric acids, the first of which, $CF_2(CN)_2$, is new. The more interesting products obtained in the three cases, respectively, were: (1) $CF_3NFC_2F_5$, $CF_3NFC_3F_7$, $C_3F_7NF_2$ and the new $NF_2(CF_2)_3NF_2$; (2) $CF_3N{=}CFC_2F_5$, $CF_3NFC_3F_7$, n-C_4F_{10}, the new n-$C_4F_9NF_2$ and cyclic $CF_2(CF_2)_3NF$; (3) $CF_3N{=}CFC_3F_7$, n-C_5F_{12}, the new n-$C_5F_{11}NF_2$, and the cyclic C_5F_{10}, $CF_2(CF_2)_3CF{=}N$ and $CF_2(CF_2)_4NF$. In the last two cases the expected linear homologs of $NF_2(CF_2)_3NF_2$ were not formed. A representative mechanism is postulated which accounts for the addition, scission, alkylation and cyclization which are observed to take place during these fluorinations.

An earlier paper of this series[3] has described the direct fluorination of cyanogen which is the simplest dinitrile. It was shown to yield not only the expected perfluoroethylenediamine, $NF_2CF_2CF_2NF_2$, and related cleavage products, but also the two perfluorinated alkylation products $(CF_3)_2NF$ and $(CF_3)_3N$. The formation of these was attributed to the intermediate production of FCN and its fluorination through the nitrene CF_3N: and the azo dimer $CF_3N{=}NCF_3$ to the alkylating radical $CF_3N{=}\dot{N}$.

This paper describes the direct fluorination in a single jet two-stage reactor of the dinitriles of perfluorinated malonic, succinic and glutaric acids, and presents a logical continuation of the earlier work on cyanogen. Each of these fluorinations yielded the anticipated cleavage and alkylation products, such as NF_3, CF_4, CF_3NF_2, C_2F_6, $(CF_3)_2NF$ and C_3F_8 in varying amounts. Also the first of these nitriles, difluoromalononitrile, $CF_2(CN)_2$, I, was prepared for the first time in 30% yield under strictly critical operating conditions by the dehydration of the corresponding amide with P_2O_5 at reduced pressure. It was easily hydrolyzed to the corresponding acid, which was identified as its known dianilinium salt.

With respect to the more important higher boiling products of these fluorinations, compound I yielded the alkylation products $CF_3NFC_2F_5$ and $CF_3NFC_3F_7$, both recently synthesized in this Laboratory,[3,4] together with n-$C_3F_7NF_2$ and the new perfluoro-1,5-diazapentane, $NF_2CF_2CF_2CF_2NF_2$ (II). Tetrafluorosuccinonitrile, $(CF_2CN)_2$ (III), was also prepared by the dehydration of the corresponding amide. Its infrared spectrum was identical with that published earlier.[5] On fluorination, III gave as alkylation products the interesting unsaturate $CF_3N{=}CFC_2F_5$ and its corresponding saturate, $CF_3NFC_3F_7$, together with the cleavage products n-C_4F_{10} and the new perfluorobutylamine, n-$C_4F_9NF_2$ (IV). However, the most important result of this fluorination was that the expected $NF_2CF_2CF_2CF_2CF_2NF_2$ was not formed, but instead cyclization occurred during the reaction which produced perfluoroazacyclopentane (perfluoropyrrolidine) $\underset{\llcorner NF \lrcorner}{CF_2CF_2CF_2CF_2}$ (V). The physical properties of this unusual compound were presented in a preliminary communication,[6] describing part of the present research. The compound IV was independently synthesized in 43 mole % yield by the direct fluorination of heptafluorobutyronitrile in order to validate its structure completely. The fluorination of hexafluoroglutaronitrile in a similar manner produced the linear unsaturate, undecafluoro-2-azahex-2-ene, $CF_3N{=}CFC_3F_7$ (VI), together with the linear cleavage products n-C_5F_{12}, and the new perfluoro-1-azahexane, n-$C_5F_{11}NF_2$ (VII). In addition, the cyclic products: C_5F_{10}, nonafluoro-1-piperideine, $\underset{\llcorner N{=}CF \lrcorner}{CF_2CF_2CF_2CF_2}$, and perfluoropiperidine, were also isolated, the last in greatest amount. Small amounts of a compound believed to be the new n-C_4F_9CN were formed in this fluorination, but sufficient quantities could not be isolated for the confirmation of its structure.

The more important physical properties of the new compounds formed in these fluorinations, together with some previously unreported physical properties of certain others, are collected in Table I.

TABLE I

PHYSICAL CONSTANTS OF COMPOUNDS

	Compound[a]	B.p., °C.	ΔH_{vap}, kcal./mole	Trouton's const., cal./deg. mole	Mol. wt.[c] Obsd.	Mol. wt.[c] Calcd.
I	$CF_2(CN)_2$	+2.0	6.84	24.9	105	102
II	$NF_2(CF_2)_3NF_2$[b]	33.0	...	...	252	254
III	$(CF_2CN)_2$	11.1	7.34	25.8	153	152
IV	n-$C_4F_9NF_2$	29.5	6.78	22.4	266	271
V	$CF_2(CF_2)_3NF$	19.3	6.5	22.2	231	233
VI	$CF_3N{=}CFC_3F_7$	39.5	...	...	274	283
VII	$C_5F_{11}NF_2$	57.5	7.8	23.6	305	321

[a] All compounds shown to be >99% pure by analytical chromatography except VI, which contained about 8% C_4F_9CN. [b] Vapor pressure curve, like that of $NF_2(CF_2)_2NF_2$, was not linear. [c] By gas density balance.

Fluorinations such as these involve not only saturation, but also cyclization, scission and alkylation, and the scheme shown illustrates a possible mechanism for the fluorination of tetrafluorosuccinonitrile III. It does not include the formation of relatively low-boiling cleavage products. Intermediates are bracketed and isolated compounds are underlined.

Inasmuch as the operating conditions in this case were not very vigorous, it is believed that the first step would be the addition of an atom of fluorine to the nitrile to give the linear monoradical indicated. This adduct could add more fluorine and then either cyclize with the expulsion of a relatively stable $\cdot NF_2$ radical leading to the formation of perfluoropyrrolidine, or else be attacked by a fluorine atom with a similar loss of

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[2] Advanced Research Projects Agency and Army Research Office (Durham) Research Associates, 1961–1962.

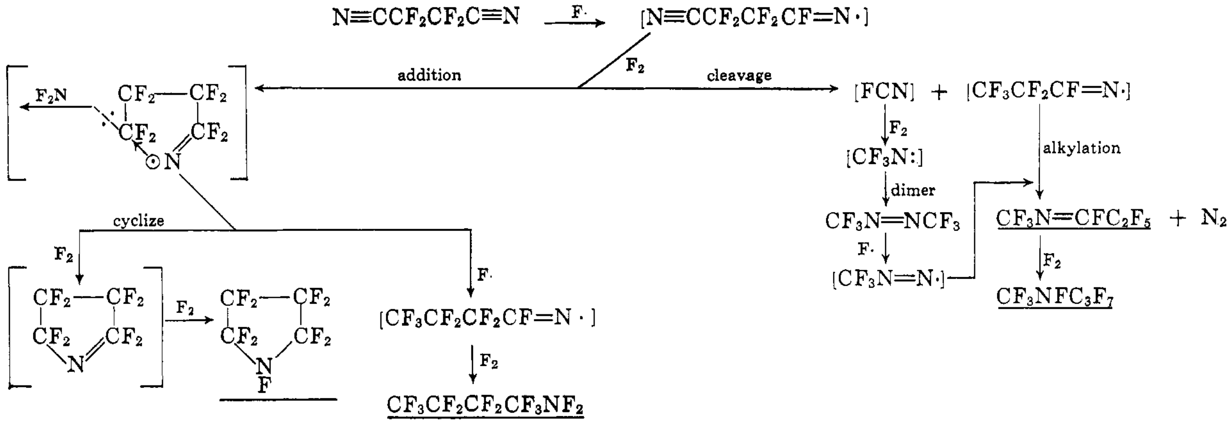
[3] P. Robson, V. C. R. McLoughlin, J. B. Hynes and L. A. Bigelow, *J. Am. Chem. Soc.*, **83**, 5010 (1961).

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

[5] D. W. Weiblen in "Fluorine Chemistry," Vol. 2, J. H. Simons, ed., Academic Press, Inc., New York, N. Y., 1954, p. 484.

[6] B. C. Bishop, J. B. Hynes and L. A. Bigelow, *J. Am. Chem. Soc.*, **84**, 3409 (1962).

THE FLUORINATION OF NC—CF_2CF_2—CN



$\cdot NF_2$ and the final production of n-$C_4F_9NF_2$. On the other hand, the original adduct might undergo cleavage with the formation of FCN and $CF_3CF_2CF{=}N\cdot$. The latter would then undergo alkylation by $CF_3N{=}N\cdot$, itself produced by the fluorination of FCN through the nitrene and azo dimer.[3] This would give first the isolated unsaturate $CF_3N{=}CFC_2F_5$ and finally its saturated analog. Similar schemes may readily be set up for the other fluorinations.

It is of interest that the fluorinated glutaronitrile yielded in addition to the well known perfluoropiperidine small amounts of the related unsaturate, nonafluoro-1-piperideine, which has been recently[7] reported. We have prepared this compound by a different route, to be described in a forthcoming publication, and fully established its structure spectroscopically. On the other hand, the fluorinated succinonitrile produced perfluoropyrrolidine, b.p. 19.5°, but none of the corresponding heptafluoro-1-pyrroline, even though the reaction was operated under considerably milder conditions. The greater resistance of the fluorinated piperideine toward free radical attack may be attributed to the fact that the six-membered ring system involves considerably less strain. However, we have shown[6] that perfluoropyrrolidine can be defluorinated to give the pyrroline boiling at 22°, which does not agree with the value of 56 to 58° reported simultaneously by Ulrich, *et al.*[7] The lower boiling point is more in line with those of the related compounds perfluorocyclopentane and octafluorocyclopentene, which boil at 23.5°[8] and 25.2°[9], respectively.

It is considered that the results which have just been described, together with those reported in the preceding three papers in the series, constitute basic information concerning the chemistry of compounds containing only carbon, nitrogen and fluorine. This field appears to be attracting increasing interest, and accordingly further work dealing with similar compounds containing both fluorine and chlorine is presently in progress.

Experimental[10]

Apparatus and Materials.—The reactors, operating techniques, chromatographic and spectroscopic apparatus used in this study have been previously described.[3,4,11]

The required $CF_2(COOC_2H_5)_2$ was donated by Pennsalt Chemicals, to whom grateful acknowledgment is hereby made. The $(CF_2COOC_2H_5)_2$ and the $CF_2(CF_2COCl)_2$ were obtained from the Columbia Organic Chemicals Co. The fluorine, rated as better than 99% pure, was furnished in cylinders by the General Chemical Co., and was used as has frequently been described.

The Synthesis of $CF_2(CN)_2$.—This new compound was prepared from $CF_2(COOC_2H_5)_2$ through the corresponding known amide[12] (15 g.), which was carefully dried and thoroughly mixed with dry sand (200 g.) and P_2O_5 (100 g.). This mixture was placed in seven Pyrex tubes (6 × 0.75 in.) which were connected by a manifold to a trap cooled in liquid oxygen and thence to a vacuum pump. The system was evacuated to 2.0 mm., after which the Pyrex tubes were quickly immersed in an oil-bath maintained at 210–220°. Difluoromalononitrile distilled from the reaction mixture as rapidly as formed, and collected in the trap. The reaction was complete in 30 min., yield 3.7 g. (30%). The pure compound boiled at +2°, mol. wt. 105 (calcd. 102), density 1.23 g./cc. at room temperature. The infrared spectrum of a gaseous sample showed an absorption band at 4.43 μ (C≡N), and the F^{19} n.m.r. spectrum exhibited only one absorption at +5.47 p.p.m. (F as CF_2), relative to CF_3COOH, in accord with the structure. The compound hydrolyzed readily to the corresponding acid, whose dianilinium salt melted at 158–160° (158–160°[13]).

The Fluorination of $CF_2(CN)_2$.—In this run the sample (23.8 g.) was metered from a cylinder at the av. flow rate of 0.022 mole/hr. into the two-stage jet reactor where it was fluorinated at the molar reaction ratio (F_2:sample:N_2) of 6.9:1:23 at 160° for 10.5 hr. to give approximately 20 cc. of crude fluorinated product, which was rectified in the usual manner with the results shown in Table II.

TABLE II

THE RECTIFICATION OF FLUORINATED $CF_2(CN)_2$

Fraction	B.p., °C.	Mol. wt.	Vol., cc.	Product
1	−124	80–89	1.5	$CF_4 + NF_3$
2	−78	119–124	2	$CF_3NF_2 + C_2F_6$
3	−38 to −35	180–185	10	Mostly C_3F_8
4	−5 to 0	210–230	3	$C_3F_7NF_2$ + some $CF_3NFC_2F_5$
5	12–14 (375 mm.)	248–260	2.5	$NF_2CF_2CF_2CF_2NF_2$ + some $CF_3NFC_3F_7$
6	. . .	. . .	1	Residue

As seen, the lower boiling fractions contained only known cleavage and alkylation products, mostly identified spectroscopically, while the higher boiling fraction 5 was separated chromatographically into $CF_3NFC_3F_7$, very recently synthesized in this Laboratory,[4] and the new $NF_2CF_2CF_2CF_2NF_2$.

Perfluoro-1,5-diaza-n-pentane, $NF_2CF_2CF_2CF_2NF_2$ (II), was isolated pure by preparative chromatography over Kel-F oil (30%) on Chromosorb-P at 20°, and the yield was 1.2 cc., or 15% based on the $CF_2(CN)_2$ used. It boiled at 33° (extrap.), with a molecular weight of 252 (calcd. 254). Its infrared spectrum showed no unsaturation and was similar to that of $NF_2CF_2CF_2NF_2$. The mass spectrum exhibited the following m/e values in order of decreasing intensity: 69 (CF_3^+), 119 ($C_2F_5^+$), 100 ($C_2F_4^+$), 31 (CF^+), 50 (CF_2^+) 114 ($C_2F_4N^+$), 52 (NF_2^+), 131 ($C_3F_5^+$), 76 ($C_2F_2N^+$) and 83 (CF_3N^+). Its F^{19} n.m.r. spectrum exhibited three absorptions at −92.6 p.p.m. (NF_2), + 39.6 p.p.m. (outer CF_2), +47.6 p.p.m. (inner CF_2), referred to CF_3COOH, with relative areas in accord with the assigned structure.

The Fluorination of $(CF_2CN)_2$.—The sample was prepared from $(CF_2COOC_2H_5)_2$ through the corresponding amide[14] by dehydra-

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

[8] W. B. Burford and R. D. Fowler, *et al.*, *Ind. Eng. Chem.*, **39**, 319 (1947).

[9] A. L. Henne and K. A. Latif, *J. Am. Chem. Soc.*, **76**, 610 (1954).

[10] Elementary analyses of the new compounds presented in this paper are not given, because of the fact that it is practically impossible to obtain from any commercial source either accurate or concordant results from volatile samples containing only carbon, fluorine and nitrogen. Instead, the structures of these compounds are established conclusively by the spectroscopic evidence presented. For a further discussion and illustrations see *J. Am. Chem. Soc.*, **81**, 3603 (1959).

[11] J. B. Hynes and L. A. Bigelow, *ibid.*, **84**, 2751 (1962).

[12] A. L. Henne and W. G. DeWitt, *ibid.*, **70**, 1548 (1948).

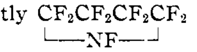
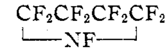
[13] D. E. M. Evans and J. C. Tatlow, *J. Chem. Soc.*, 3779 (1954).

[14] A. L. Henne and W. F. Zimmer, *J. Am. Chem. Soc.*, **73**, 1103 (1951).

tion over P_2O_5 in a manner similar to that just described, in an average yield of 9%. Much of the remaining product appeared to be the corresponding imide. The nitrile was a colorless liquid, b.p. 11.1°, mol. wt. 153 (calcd. 152), with an infrared spectrum identical with that published earlier.[5] The $(CF_2CN)_2$ (27.0 g.) was metered from a cylinder at the av. flow rate of 0.036 mole/hr. into the reactor and fluorinated at the molar reaction ratio of 4.2:1:14 at 145° for 5 hr. to give about 23 cc. of crude product, which was rectified in the usual manner, with the results shown in Table III.

TABLE III

THE RECTIFICATION OF FLUORINATED $NC{-}CF_2CF_2{-}CN$

Fraction	B.p., °C.	Mol. wt.	Vol., cc.	Product
1	−120 to −95	74–85	3.5	$CF_4 + NF_3$
2	−76 to −74.5	120–145	2.3	Mostly C_2F_5 + trace CF_3NF_2
3	−36	172–183	2.2	$C_3F_8 + (CF_3)_2NF$
4	0 to 11	234–238	7	Mostly n-C_4F_{10} + $CF_3N{=}CFC_2F_5$
5	0 to 3 (383 mm.)	238–241	5	Mostly  $\underbrace{CF_2CF_2CF_2CF_2}_{NF}$ + $CF_3N{=}CFC_2F_5$ + $CF_3NFC_3F_7$
6	Residue		3	n-$C_4F_9NF_2$ +  $\underbrace{CF_2CF_2CF_2CF_2}_{NF}$

Again the lower boiling fractions contained only known and readily identified cleavage products. The higher boiling fractions were resolved chromatographically in the usual manner, yielding the cleavage products n-C_4F_{10} and the new n-$C_4F_9NF_2$, b.p. 29.5°, together with the interesting unsaturate $CF_3N{=}CFC_2F_5$ and its corresponding saturate $CF_3NFC_3F_7$, both recently synthesized in this Laboratory.[4] The most significant product, perfluoropyrrolidine, was isolated in pure condition from fraction 5 by preparative chromatography.

Perfluoroazacyclopentane, C_4F_9N (V), was a colorless liquid (5 cc.), b.p. 19.3° (extrap.), av. mol. wt. 231 (calcd. 233), obtained in about 20 mole % yield assuming density as 1.70. The infrared spectrum exhibited its most intense absorption at 10.26 μ and was similar to that of perfluorocyclopentane. Its F^{19} n.m.r. spectrum exhibited three absorptions at +33.0 p.p.m. (αCF_2), +42.1 p.p.m. (NF) and +52.2 p.p.m. (βCF_2) referred to CF_3COOH, with relative areas in accord with the assigned structure.

Perfluoro-n-butylamine, n-$C_4F_9NF_2$ (IV), was found by its infrared spectrum to be identical with similar material synthesized as follows.

Commercial C_3F_7CN (55 g.) was fluorinated at the av. flow rate of 0.0186 mole/hr. and reaction ratio of 6.7:1:16 at 173–180° for 9 hr. to give about 46 cc. of crude product. On distillation this gave almost entirely n-C_4F_{10} and n-$C_4F_9NF_2$. Redistillation of the higher boiling materials (b.p. > 0°) in a vacuum-jacketed column packed with glass helices yielded a fraction, b.p. 30–33° (14 cc.), corresponding to a 43 mole % yield of $C_4F_9NF_2$ assuming its density to be 1.70 g./cc. After further purification by preparative chromatography it was found to be a colorless liquid, b.p. 29.3° (extrap.), av. mol. wt. 266 (calcd. 271). Its infrared spectrum indicated no unsaturation, and its F^{19} n.m.r. spectrum exhibited five absorptions at −92.6 p.p.m. (NF_2), +5.5 p.p.m. (CF_3), +40.6 p.p.m. (αCF_2), + 47.4 p.p.m. (βCF_2) and +50.5 p.p.m. (γCF_2), all referred to CF_3COOH, with relative areas in accord with the assigned structure.

The Fluorination of $CF_2(CF_2CN)_2$.—The sample was prepared from $CF_2(CF_2COCl)_2$ by conversion to the corresponding amide, followed by dehydration by the method described by McBee.[15] The nitrile was a colorless liquid, b.p. 39°, with an intense infrared absorption at 4.42 μ ($C{\equiv}N$). The $CF_2(CF_2CN)_2$ (28.1 g.) was carried on nitrogen from a saturator maintained at 0° into the reactor at the average flow rate of 0.0186 mole/hr., and fluorinated at the molar reaction ratio of 9.7:1:34 at 150° for 7.5 hr. to give about 18 cc. of crude product. This material was then subjected to a trap-to-trap distillation, giving a fraction (6 cc.) which boiled below room temperature, and a higher boiling fraction (12 cc.). The former was shown chromatographically and by infrared spectroscopy to contain n-C_5F_{12} together with smaller amounts of n-C_4F_{10}, C_5F_{10} (cyclic) and n-C_4F_9CN. Also, the usual low boiling cleavage and alkylation products were undoubtedly present. Perfluorovaleronitrile, n-C_4F_9CN, was tentatively identified by its infrared spectrum which showed an absorption at 4.41 μ ($C{\equiv}N$), but could not be isolated in significant amount. The higher boiling fraction was shown to contain, in the order of volatility, C_5F_{10} (cyclic, trace), n-C_5F_{12}, n-C_4F_9CN (trace), $CF_3N{=}CFC_3F_7$, perfluoropiperidine (2 cc.), nonafluoro-1-piperideine (trace) and the new $C_5F_{11}NF_2$, b.p. 57.5° (extrap.), together with a little unreacted dinitrile.

Undecafluoro-2-azahex-2-ene, $CF_3N{=}CFC_3F_7$ (VI), (0.6 cc.) was a colorless liquid, 92% pure by analytical chromatography, the contaminant being n-C_4F_9CN, which could not be separated. It boiled at 39°, mol. wt. 274 (calcd. 283). The infrared spectrum of a pure sample obtained by analytical chromatography showed an absorption at 5.62 μ ($C{=}N$). The F^{19} n.m.r. spectrum exhibited five absorptions at −52.5 p.p.m. (CF), −17.8 p.p.m. (CF_3 on N), +5.5 p.p.m. (CF_3 on CF_2), +42.3 p.p.m. (CF_2 on $CF{=}$) and +50.9 p.p.m. (CF_2 on CF_3). With the exception of the −17.8 p.p.m. absorption, these shifts are in agreement with those reported earlier[16] for this compound. It is believed that the chemical shift of the CF_3 group bound to nitrogen (−36 p.p.m.) reported by these investigators is in error, since similar compounds containing a CF_3 group bound to an unsaturated nitrogen atom exhibit a peak near −18 p.p.m.[17] On hydrolysis with 10% NaOH at room temperature it yielded NH_3, Na_2CO_3 and n-C_3F_7COONa, the latter being identified by its infrared spectrum.

Perfluoro-1-azahexane $C_5F_{11}NF_2$ (VII), (0.5 cc.) was a colorless liquid chromatographically pure, b.p. 57.5° (extrap.), mol. wt. 305 (calcd. 321). Its infrared spectrum showed no unsaturation and was otherwise consistent. The F^{19} n.m.r. spectrum exhibited absorptions at −92.4 p.p.m. (NF_2), +5.8 p.p.m. (CF_3), +39.7 p.p.m. (αCF_2), +46.8 p.p.m. (β + γCF_2's unresolved) and +50.0 p.p.m. (δCF_2), the relative areas of which were in qualitative accord with the assigned structure.

Acknowledgment.—We are indebted to Dr. Wallace S. Brey, University of Florida, for the F^{19} n.m.r. spectra presented here.

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[15] E. T. McBee, P. A. Wiseman and G. B. Bachman, *Ind. Eng. Chem.*, **39**, 415 (1947).

[16] N. Muller, P. C. Lauterbur and S. F. Svatos, *J. Am. Chem. Soc.*, **79**, 1807 (1957).

[17] W. S. Brey, private communication.