[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Organic Compounds. XXI. The Fluorination of Malononitrile and Dimethyl Formamide[1]

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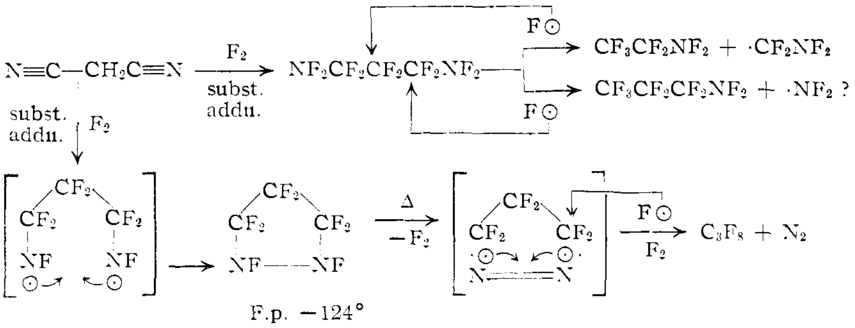
Malononitrile and dimethyl formamide have been fluorinated over a metal packing under a variety of conditions. In addition to the expected lower boiling fragments, less volatile highly fluorinated products have been obtained in significant yields, which on rectification yielded two new compounds to which the structures $\underbrace{CF_2CF_2CF_2NFNF}$ and $CHF_2NF{-}NFCF_3$ have tentatively been assigned, the former coming from the nitrile, and the latter from the amide. Good evidence has been presented to indicate that completely fluorinated malononitrile and perfluoro-*n*-propylamine, admixed with their isomers, were also formed and that the fluorination of dimethyl formamide produces a good yield of pure $(CF_3)_2NF$, unaccompanied by its isomer. The free radical mechanisms of these fluorinations have been discussed in some detail.

This paper describes the direct fluorination over a copper metal packing under many different conditions of the commercially available compounds $CH_2(CN)_2$ and $HCON(CH_3)_2$. The first of these was selected in order to extend earlier studies[4] on the fluorination of nitriles and also, since its unknown completely fluorinated derivative, $NF_2CF_2CF_2CF_2NF_2$, represented a new and interesting series of perfluorinated organic compounds containing both carbon and nitrogen. The second compound was chosen as a natural extension of our earlier work[5] dealing with the fluorination of amines.

In the preceding papers it has been shown that the fluorination of organic compounds containing nitrogen usually leads to the formation of five crude products boiling near: (1) −128° (CF_4), (2) −80° (C_2F_6 + CF_3NF_2), (3) −40° ($CF_3CF_2NF_2$ + $(CF_3)_2NF$), (4) roughly −20° (1 atm.) to 0° (200 mm.) (volatile higher boiling material) and (5) an intractable residue. The nitrile and amide presently under study yielded varying amounts of all of these except two; it appears significant that no appreciable amounts of either C_2F_6 or CF_3NF_2 were formed in either of these fluorinations. It was also clear that in both cases new highly fluorinated organic products containing nitrogen and possessing interesting structures would be found only in fraction 4, which constituted roughly 15–20 liquid volume per cent. of the product in both cases.

In the fluorination of malononitrile it was found that fraction 3 consisted for the most part of C_3F_8 (b.p. −36°), and this fact supports the structure of the cyclic intermediate proposed below. The accumulated fraction 4 in this instance, on very careful rectification, yielded an analytically pure cut (10 cc.), b.p. −35.5° at 203 mm., f.p. −124° (sharp), mol. wt. 207, to which the structure $\underbrace{CF_2CF_2CF_2NFNF}$ (mol. wt. calcd. 216) has been tentatively assigned. There were also formed a portion (7 cc.), b.p. −30.5 to −30° at 203 mm., mol. wt. 220 ($CF_3CF_2CF_2NF_2$ or isomer, mol. wt. calcd. 221), and a further significant fraction (16 cc.), b.p. −7 to +4° at 203 mm., mol. wt. 258 (completely fluorinated malononitrile or perfluoro-1,3-diaminopropane, $NF_2CF_2CF_2CF_2NF_2$, mol. wt. calcd. 254). These materials, which had constant molecular weights but did not freeze well, were considered to be non-azeotropic mixtures of one or more isomers.

The formation of all of these products may readily be explained on the basis of free radical reactions according to the postulated mechanism.



Obviously the fluorinolysis and cyclization could and probably did in part take place before the reaction had reached the perfluorinated stage shown above. The cyclic azo intermediate, while not actually isolated, would be much more sterically favored than that proposed earlier[5] to explain the fluorination of ethylenediamine. At that time it was shown that fluorine could not be added directly to an azo linkage, and therefore the loss of fluorine to produce this structure as postulated above does not seem to be too far out of line. The attack of fluorine upon this molecule to form C_3F_8 and N_2 compare well with the observed fluorinolysis of $CF_3N{=}NCF_3$ at high temperature described earlier.

In the corresponding fluorination of dimethyl formamide it appeared that fraction 3 consisted

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[1] This material was presented at the September, 1954, Meeting of the American Chemical Society in New York and has been constructed in part from portions of the Doctorate Thesis presented by Jay A. Gervasi to Duke University in February, 1954.

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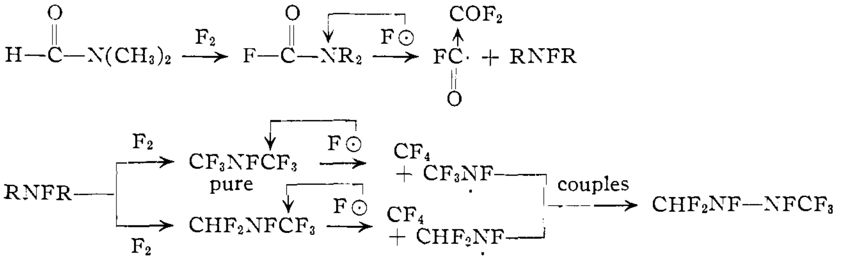
[4] J. A. Cuculo and L. A. Bigelow, THIS JOURNAL, **74**, 710 (1952).

[5] J. A. Gervasi, M. Brown and L. A. Bigelow, *ibid.*, **78**, 1679 (1955).

essentially of pure $(CF_3)_2NF$, unaccompanied by appreciable amounts of its isomer $CF_3CF_2NF_2$. The accumulated fraction 4 in this case on distillation yielded a significant crude cut (13 cc.), b.p. −16 to −15°, mol. wt. 183–187, which on repeated rectification gave a nearly analytically pure sample (2 cc.) b.p. −15°, f.p. −123° (sharp), mol. wt. 187 constant, to which the structure $CHF_2NF\text{–}NFCF_3$ (mol. wt. calcd. 186) has been tentatively assigned. Material was also obtained boiling near +15°, mol. wt. not far from 200, but it could not be completely purified. Perfluorodimethyl formamide, $FCON(CF_3)_2$, has mol. wt. calcd. 199. It was also significant that no appreciable amounts of either C_2F_6 or the known $(CF_3)_2N\text{–}N(CF_3)_2$ could be isolated from among the products of this fluorination. The latter compound appears in considerable amount in the fluorination of dimethylamine.

All of these results may readily be explained according to the postulated sequence



R = $—CH_3$, $—CH_2F$, $—CHF_2$ or $—CF_3$

Here the fluorinolysis has been represented as taking place prior to the perfluorinated stage, since the final product was not perfluorinated. It must almost certainly take place by an attack upon nitrogen, displacing the highly resonant and stable $F\dot{C}{=}O$ radical, instead of the usually preferred attack upon carbon. Had the attack been upon carbonyl carbon, $\cdot NR_2$ radicals would have been displaced, and $(CF_3)_2N\text{–}N(CF_3)_2$ ultimately produced; if alkyl rather than acyl groups had been displaced, C_2F_6 would have been formed. However, as stated above, neither of these compounds appeared in appreciable amounts among the products of this fluorination. This interpretation also leads to the conclusion that the $(CF_3)_2NF$ produced must be, as it was, essentially uncontaminated by its isomer. It is also of interest that a portion having the same characteristics as the present $CHF_2NF\text{–}NFCF_3$ was formed during the fluorination in the jet reactor of ethylene imine, as described in the preceding paper.[5] This product was not recognized at that time but obviously could have been formed quite easily by the fluorination of the imine through the intermediate R–NF–R followed by fluorinolysis and dimerization as above.

The constitution and properties of the so-called volatile higher boiling products which have been described in this and the preceding paper would seem to constitute an interesting and relatively unexplored corner of fluorine chemistry. Further work along these lines is now in progress in this Laboratory.

Experimental

Apparatus.—Two different fluorination reactors were used in these studies, the L-[6] and the T-types.[7] In the fluorination of malononitrile, the metal-packed L-reactor was placed horizontally with the unpacked side-arm extending directly upward. This side-arm was fitted with a short section of copper tubing leading to a glass to metal seal and glass sleeve. The liquid sample was admitted through a vertical buret provided with a calibrated glass capillary adaptor, through which it dropped directly into the side-arm through the sleeve. All glass connections were made tight by Tygon tubing. Metered diluent nitrogen was simultaneously admitted below the capillary, with a by-pass to the top of the buret to maintain equal pressure, while the buret and fittings were held close to 40° by a warm air spray from a perforated and heated copper tube coil in order to keep the nitrile (m.p. 32°) in the liquid state. Metered fluorine was admitted through the end next to the side arm, while the products passed out at the opposite end. In the fluorination of dimethyl formamide the T-reactor was employed in the conventional manner.

Materials.—Commercial malononitrile, stated b.p. 110–111° at 18 mm., was redistilled at reduced pressure before use; while commercial dimethyl formamide was redistilled, b.p. 153°.

The Fluorination of Malononitrile.—At first a series of preliminary runs was made and the approximate results of these are presented below in Table I. The typical operating procedure was as follows. Liquid malononitrile at 38° was dropped from a buret through a capillary, calibrated in position during the run, at the rate of 0.051 mole/hr. directly into the L-reactor maintained at a reaction temperature of 250°, where it met and reacted with fluorine diluted with nitrogen so that the approximate molar reaction ratio (F_2:nitrile:N_2) was 3:1:9, corresponding to a fluorination ratio of 3:1 and a dilution ratio of 1:3 (±10%). The products were passed over NaF pellets at 100° and then condensed by Dry Ice and liquid air. After 10 hr. 32 cc. of crude product had collected, the volatile portion of which (26.5 cc.) was passed through a solution of 5% NaOH + 5% $NaHSO_3$ in a countercurrent flow apparatus, yielding finally 22 cc. of stabilized product, which was then rectified in a Booth–Podbielniak precision still, with the results shown in Table I, run 5.

TABLE I

THE RECTIFICATION OF FLUORINATED MALONONITRILE

		Liquid volume % of total condensate of crude					
Run	Approx. molar reaction ratio F_2:nitrile:N_2	CF_4	CF_3NF_2 + C_2F_6	CF_3-CF_2-NF_2 + C_3F_8	Volatile higher boiling (V.H.B.)	Stabln. loss	Nonvolatile residue
1	3:1:9	17	6	25	21	1	22
2	4:1:12	22	7	20	20	..	19
3	5:1:15	22	5	30	14	[a]	20
4	6:1:18	27	8	33	14	0	17
5	3:1:9	18	5	22	16	14	17

[a] This run was not stabilized before distillation.

Run 1.—The volatile higher boiling fraction (V.H.B.) on rectification yielded a portion (1.3 cc.), b.p. −8 to −1° (207 mm.), mol. wt. 258; calcd. for $NF_2CF_2CF_2CF_2NF_2$ and/or isomers (A) 254.

Run 2.—V.H.B. on redistillation gave a portion (3 cc.), b.p. −1 to 0° (1 atm.), mol. wt. 220–226; calcd. for $CF_3CF_2CF_2NF_2$ and/or isomer (B) 221.

Run 3.—V.H.B. in this case on fractionation yielded two significant cuts: the first (4 cc.), b.p. −20 to −15°, mol. wt. 178–179; and the second (1.4 cc.), b.p. −2 to −1° at 207 mm., mol. wt. 251–258; calcd. for $\underbracket{CF_2CF_2CF_2N{=}N}$ mol. wt. 179; and for A, mol. wt. 254.

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(6) F. F. Holub and L. A. Bigelow, THIS JOURNAL, **72**, 4879 (1950).

(7) A. R. Gilbert and L. A. Bigelow, *ibid.*, **72**, 2411 (1950).

The lower boiling fractions were combined, stabilized over 5% NaOH + 5% $NaHSO_3$, and on fractionation yielded a portion (11 cc.), b.p. −40 to −37°, mol. wt. 176–204, which on refractionation gave a portion (10 cc.), b.p. −64 to −63° (200 mm.), mol. wt. 181–189, which was nearly all C_3F_8, and from which was separated pure C_3F_8 (6 cc.), mol. wt. 189, calcd. 188.

Run 5.—V.H.B. on rectification yielded three significant cuts; (a) (1.8 cc.), b.p. −35 to −32° (207 mm.), mol. wt. 206; (b) (1.1 cc.), b.p. −31 to −27° (207 mm.), mol. wt. 221–226; (c) (1.6 cc.), mol. wt. 258; calcd. for $\underline{CF_2CF_2CF_2NFN}F$, mol. wt. 216; for B, mol. wt. 221; for A, mol. wt. 254.

Large Scale Run.—The operating procedure here was as above, with sample flow rate 0.035 mole/hr.; reaction temperature 250°, base temperature 240°; reaction ratio 3:1:9; operating time 71.4 hr.; crude product 195 cc.; volatile product 161 cc.; stabilized product 142 cc. Rectification in the usual manner gave the following results where the figures represent crude material including minor products and transitions: CF_4, 13%; b.p. −95 to −84°, 8%; C_3F_8 + $CF_3CF_2NF_2$, 30%; *volatile higher boiling, 22%;* stabilization loss, 10%; and non-volatile residue, 18%. The volatile higher boiling portion, b.p. −19° (1 atm.) to −1° (207 mm.), contained all the interesting products with molecular weights concentrated near 260 (18 cc.), 225 (16 cc.) and 205 (8 cc.). These portions were then combined with similar material from all previous runs and refractionated with great care.

The material, mol. wt. near 260, yielded a portion (3 cc.), b.p. −9 to −7° at 203 mm., mol. wt. 250, and another portion (16 cc.), b.p. −7 to +4° at 203 mm., mol. wt. 258. These products which were not changed by further stabilization and did not freeze well, appeared to be mixtures of isomers; completely fluorinated malonitrile, $NF_2CF_2CF_2CF_2NF_2$, or isomers, mol. wt. (calcd.) 254.

The material, mol. wt. near 225, yielded a portion (7 cc.), b.p. −30.5 to −30° at 203 mm., mol. wt. 220, and another portion (3 cc.), b.p. −29.5 to −25° at 203 mm., mol. wt. 223. These products did not freeze well and appeared to be mixtures of isomers; perfluoro-*n*-propylamine, $CF_3CF_2CF_2NF_2$ or isomer, mol. wt. (calcd.) 221.

Finally the material, mol. wt. near 205, yielded a central cut (14.5 cc.), b.p. −35° at 203 mm., f.p. −132° (fair), mol. wt. 204. This was again refractionated, yielding another central cut (10 cc.), b.p. −35.5° at 203 mm., f.p. −124° (sharp), mol. wt. 207. The unknown $\underline{CF_2CF_2CF_2NFN}F$ has mol. wt. (calcd.) 216.

Anal. Calcd. for $C_3N_2F_8$: F, 70.4. Found: F, 70.2.

The Fluorination of Dimethyl Formamide.—Altogether thirteen significant runs were made under many conditions and in three different reactors, the approximate results of the most representative of these, in all of which the T-reactor was used, are presented below in Table II. The typical operating procedure was as follows. The dimethyl formamide, diluted with 7 l./hr. of nitrogen, was carried from the saturator, heated to 80°, at the rate of 0.032 mole/hr. into the T-reactor maintained at 115°, where it met and reacted with 0.29 mole of fluorine carried in on 14.3 l./hr. of nitrogen, such that the molar reaction ratio was 9:1:27. The exit gases were passed over NaF pellets at 100° and then condensed by Dry Ice and liquid air. After 16 hr. 70 cc. of crude product had collected, the volatile portion of which (65 cc.) was passed through a solution of 3% NaOH + 5% $NaHSO_3$ in a countercurrent flow apparatus, yielding finally 46 cc. of stabilized product, which was then rectified in a Booth–Podbielniak precision still. The presence of large amounts of subliming solid which had to be drawn off interfered seriously with the distillation from −120° to −70°. The results are shown below in Table II, run 3.

TABLE II

THE RECTIFICATION OF FLUORINATED DIMETHYL FORMAMIDE

Run	Ratio	Temp., °C.	Liq. vol. % of volatile stabld. condensate of crude CF_4	Subliming solid	$(CF_3)_2NF$	Volatile higher boiling
1	7:1:21	115	23	19[a]	31	27
2	8:1:24	115	30	38	12	20
3	9:1:27	115	13	50	24	14
4	6:1:24	125	23	9[a]	36	32
5	7:1:21	125	17	35[a]	28	21
6	7:1:28	125	34	34[b]	14	19
7	8:1:24	200	9	59	26	7
8	10:1:24	275	7	58	26	9

[a] Stabilized by 3% NaOH only. [b] This run not stabilized; this figure represents crude COF_2.

The subliming solid which appeared in all stabilized runs was accumulated, stored in a cylinder, finally purified in a specially designed sublimation unit and yielded a portion, mol. wt. 44–46, the infrared spectrum of which indicated CO_2 (mol. wt. calcd. 44) and an unknown contaminant. The former could have resulted from the hydrolysis of much COF_2 and so passed through the stabilizer; while the latter could possibly have been FCN, although none of this compound was isolated from the unstabilized runs.

Run 1.—The volatile higher boiling fraction contained a portion (3 cc.), b.p. −15°, mol. wt. 202, which froze sharply at −142°.

Run 2.—This run was repeated (24 hr., not stabilized) and the volatile higher boiling fraction contained a portion (10 cc.), b.p. −14 to +18°, which on refractionation yielded two cuts, one (4 cc.), b.p. −14 to −13°, mol. wt. 195–197; the other (4 cc.), b.p. 7 to 8° (600 mm.), mol. wt. 208.

Run 5.—In this run the $(CF_3)_2NF$ was shown to be pure, b.p. −39°, f.p. −170° (sharp), mol. wt. 173 (known b.p. −37°,[8] f.p. −171°,[4] mol. wt. calcd. 171).

Large Scale Run.—The operating procedure here was as above, with the sample carried into the T-reactor at 0.032 mole/hr., where it met and reacted with 0.256 mole of fluorine carried in on 0.768 mole/hr. of N_2, such that the reaction ratio was 8:1:24, the temperature was 115°; operating time 82 hr.; crude product 315 cc.; volatile product (235 cc.), which was rectified in the usual manner without stabilization, yielding the following crude products: CF_4, 19%; COF_2, 45%; $(CF_3)_2NF$, 24%; and volatile higher boiling, 12%. The last fraction contained a portion (13 cc.), b.p. −16 to −15°, mol. wt. 183–187. This was stabilized by 5% NaOH + 1% $NaHSO_3$ and redistilled yielding a product (10 cc.), b.p. −16 to −15°. This was again distilled yielding a central cut (6 cc.), b.p. −15°, mol. wt. 187–191, which was again distilled yielding another central cut (4 cc.), b.p. −15°, f.p. −124 to −123°, mol. wt. 187, which was once more redistilled yielding a pure central cut (2 cc.), b.p. −15°, f.p. −123° (sharp), mol. wt. 187 constant. Further redistillation of this product produced no change in physical properties. The compound $CHF_2NF{-}NFCF_3$, or isomer, has mol. wt. (calcd.) 186.

Anal. Calcd. for $C_2HN_2F_7$: F, 71.5. Found: F, 72.3.

This result is not regarded as wholly satisfactory, but on account of the great technical difficulties involved in such an analysis, it may be considered to have reasonable significance.

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[8] J. Thompson and J. H. Emeleus, *J. Chem. Soc.*, 3080 (1949).