tion was slower. Figure 1 shows the volume of gas absorbed, plotted against time for 1-hexene and 2-hexene.[10]

Identification of Reaction Products.—A solution of hydrocarbonyl in hexane was prepared as above except that 4.9 mmoles of $Co_2(CO)_8$ was used. The spectrum of the hydrocarbonyl in the 4.4 to 5.6 μ region is shown in Fig. 2A. To this solution there was then added 20 ml. of 1-hexene. Gas absorption commenced immediately and was complete when 1.03 mmoles of carbon monoxide per 2 mmoles of hydrocarbonyl (6 min.) was absorbed. The solution was cooled to Dry-Ice temperature and the precipitated dicobalt octacarbonyl filtered and air-dried (0.9 g., 81% of theory). Recrystallization gave material of m.p. 51–52°. The infrared spectrum in hexane (Fig. 2b) was identical with authentic dicobalt octacarbonyl. After removal of the dicobalt octacarbonyl, the infrared absorption spectrum of the filtrate was determined. The 4.4–5.6 μ portion of this spectrum is shown in Fig. 2C. It will be noted that in the region shown, the broad band which appears in the 4.9 μ region in both hydrocarbonyl and octacarbonyl has been resolved into several sharp bands. The significance of this change is under study. The spectrum of the reaction mixture also showed bands at 5.8 (heptaldehyde), 5.5 and 6.1 (1-hexene), 10.1 (1-hexene), 10.38 (2-hexene), 10.98 (1-hexene), 14.4 μ (2-hexene). The absence of appreciable absorption at 5.4 and 14.2 μ indicated that neither much octacarbonyl nor hydrocarbonyl was present. Chemical tests (nickel *o*-phenanthroline) also indicated the absence of these carbonyls. An aliquot of the reaction mixture was analyzed by gas chromatography using a silicone column. Comparison with a known mixture of hexane, 1-hexene and 2-hexene showed that the reaction mixture contained approximately 65% 1-hexene, 20–25% 2-hexene and the balance (10–15%) probably 3-hexene. The balance of the reaction mixture was treated with an alcoholic solution of 2,4-dinitrophenylhydrazine to which a few drops of sulfuric acid had been added. After refluxing for several hours, followed by cooling, the precipitated crystals were separated. These melted over a wide range with complete melting below 100°. Recrystallization did not improve the melting point. It was assumed that the crystals were a mixture of hydrazones from various C-7 aldehydes. *Anal.* Calcd. for $C_{13}H_{18}N_4O_4$: C, 53.05; H, 6.17. Found[11]: C, 52.51; H, 6.01. The formation of octacarbonyl according to the reaction scheme proposed here should coincide with the disappearance of a complex and the appearance of product aldehyde. Qualitative data on the rate of aldehyde formation could not be secured owing to experimental difficulties with the small quantities involved.

Equivalence of Hydrocarbonyl Disappearance and Carbon Monoxide Absorption.—The reaction of hydrocarbonyl with 1-hexene was carried out as described above but at 0°. At this temperature gas absorption took several hours. After 1.2 mmoles of carbon monoxide had been absorbed, the mixture was analyzed for remaining hydrocarbonyl by nickel *o*-phenanthroline precipitation[12] and 1.5 mmoles of $HCo(CO)_4$ was found (theory, 1.6 mmoles based on amount of carbon monoxide absorbed).

Reaction of Isoprene with Cobalt Hydrocarbonyl.—To a solution of 4 mmoles of $HCo(CO)_4$ in 16 ml. of decalin at 25° there was injected 3 ml. (30 mmole) of isoprene (99.8% isoprene by vapor fractometer analysis[13]); 50 ml. of gas was evolved in 0.5 hour. The solution was cooled to $-78°$ in a Dry Ice-bath and the low-boiling olefin distilled at a pressure of 2 mm. as the olefin warmed up to room temperature. Vapor fractometer[13] analysis revealed 1% 2-methyl-2-butene in the isoprene which corresponds to an approximately 16% yield of product.

Acknowledgment.—The authors wish to thank the Houdry Process Corporation for a generous fellowship which made this work possible, and Drs. G. Alex Mills and Sol Weller for stimulating discussions. The authors also wish to thank Bernard Krabacher for valuable technical assistance.

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[10] Several dozen experiments on carbon monoxide absorption by 1-hexene in hexane containing cobalt hydrocarbonyl indicated that the carbon monoxide absorption was slightly greater on the average than the ratio $2HCo(CO)_4{:}1CO$, possibly due to slight decomposition of complexes.

[11] Geller Laboratories, Bardonia, N. Y.

[12] H. Sternberg, I. Wender and M. Orchin, *Anal. Chem.*, **24**, 174 (1954).

[13] Analysis by the Analytical Division, The Houdry Process Corp.

CINCINNATI 21, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Organic Compounds. XXII. The Fluorination of Some Amides, Nitriles and of Methyl Thiocyanate[1]

BY JOHN A. ATTAWAY,[2a] RICHARD H. GROTH[2b] AND LUCIUS A. BIGELOW

RECEIVED NOVEMBER 29, 1958

The substituted amides $HCON(CH_3)_2$ and $HCONHCH_3$ were cleaved when fluorinated under vigorous conditions. The former yielded pure $(CF_3)_2NF$ (38%), $(CF_3)_3N$ and $(CF_3)_2N{-}N(CF_3)_2$; while the latter gave $CF_2{=}NF$, CF_3NF_2 and $(CF_3)_2NF$. Unsubstituted acetamide under mild conditions was cleaved even before the replacement of hydrogen atoms, giving CH_3COF (52%) and elementary nitrogen. The perfluoronitriles CF_3CN and CF_3CF_2CN when fluorinated under very mild conditions yielded the new perfluoroazo compounds $CF_3CF_2N{=}NCF_2CF_3$ and $CF_3CF_2CF_2N{=}NCF_2CF_2CF_3$, while CF_3CF_2CN under vigorous conditions gave pure $CF_3CF_2CF_2NF_2$ not previously fully reported. Finally, methyl thiocyanate, CH_3SCN, under mild conditions gave the new SF_5CN, and under vigorous conditions the new $SF_5CF_2NF_2$, along with much SF_6 and other products. Possible mechanisms for these reactions have been presented.

This paper describes the results of the direct fluorination of three not entirely unrelated classes of organic compounds containing either nitrogen or both nitrogen and sulfur as so-called additional elements. In an earlier report from this Laboratory[3] it was stated that in the direct fluorination of N-dimethylformamide under relatively mild conditions the primary attack of the fluorine which led to fluorinolysis was directly upon the nitrogen atom at least for the most part, since $(CF_3)_2NF$ was produced in good yield while none of the dimer $(CF_3)_2N{-}N(CF_3)_2$ could be isolated from the product. This fluorination has now been repeated under more vigorous conditions and, for example, at the molar

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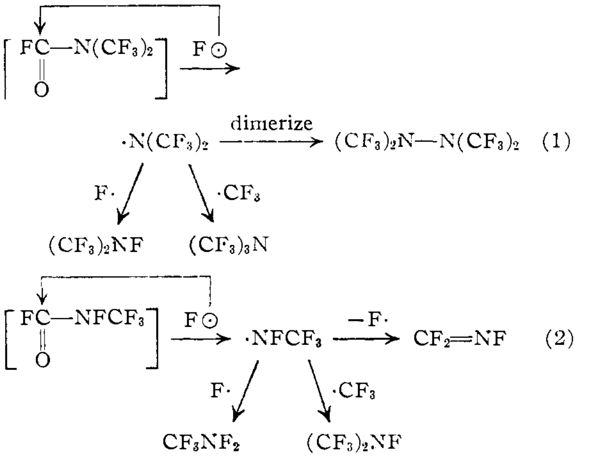
[1] This material was presented at the September, 1956, Meeting of the American Chemical Society in Atlantic City, N. J., and has been abstracted in part from the Doctorate Thesis presented by John A. Attaway to Duke University in January, 1957.

[2] (a) Research Assistant, Office of Ordnance Research, Summer, 1954; Office of Naval Research, 1954–1955, Fall, 1956; Allied Chemical and Dye Corporation Fellow, 1955–1956. Grateful acknowledgment is also made to the Duke University Research Council for a grant. (b) Post-doctorate Research Associate, Office of Naval Research, 1956.

[3] F. P. Avonda, J. A. Gervasi and L. A. Bigelow, THIS JOURNAL, **78**, 2798 (1956).

reaction ratio (F_2:sample:He) of 12:1:24 and 275°, there were formed in significant amounts, $(CF_3)_2NF$, $(CF_3)_3N$ and $(CF_3)_2N\text{-}N(CF_3)_2$ accompanied by the usual CF_4, COF_2 and other products. These results indicate that the fluorinolysis must have taken place in considerable amount at least by carbonyl group attack leading to the direct formation of $\cdot N(CF_3)_2$ radicals. These, in turn, either accepted fluorine atoms to give $(CF_3)_2NF$, $\cdot CF_3$ radicals to give $(CF_3)_3N$, or dimerized to the hydrazine. The $\cdot CF_3$ radicals necessary for the alkylation to $(CF_3)_3N$ may have resulted from the pyrolysis of either $(CF_3)_2N\text{-}N(CF_3)_2$ or $CF_3N{=}NCF_3$ at the very high temperatures along the flame fronts always present in a T-reactor[4] during a fluorination. It should be stated, however, that the pure compounds by themselves have been shown not to crack at temperatures of 440° (long pass) and 500° (short pass), respectively. The $(CF_3)_2NF$ formed was pure, contained none of the isomeric $CF_3CF_2NF_2$, and could be obtained in 38% yield under slightly more vigorous operating conditions. It is recognized, of course, that the cleavage just described may have taken place either before or after all of the hydrogen atoms in the molecule had been replaced by fluorine. No more than traces of perfluoro-N-dimethylformamide $(CF_3)_2NCOF$ appear to have been formed at any time.

Since the preceding fluorination had led to the formation of the hydrazine dimer, it appeared possible that a new and very interesting dimer, $CF_3NF\text{-}NFCF_3$ might result from the fluorination of N-methylformamide under similar conditions. Although this did not prove to be the case, the fluorination of $HCONHCH_3$ did give some interesting information which appeared to indicate that here also the cleavage took place to a great extent at least by carbonyl group attack. For example, at the reaction ratio of 10:1:20 and 275° there were formed in significant amounts: impure $CF_2{=}NF$, CF_3NF_2 and $(CF_3)_2NF$, accompanied by CF_4, COF_2 and other products. The cleavage led to the formation of $\cdot NFCF_3$ radicals, which lost fluorine atoms to give $CF_2{=}NF$; reacted with fluorine to give CF_3NF_2; or accepted $\cdot CF_3$ radicals to form $(CF_3)_2NF$. While the dimer $CF_3NF\text{-}NFCF_3$ was not isolated, it may have been decomposed into the stable $CF_3N{=}NCF_3$, and this in turn could have been present in the $(CF_3)_2NF$ as a contaminant. As before, none of the perfluoro amide was obtained. The essential portions of the mechanisms involved are represented by the scheme shown.



Some interesting experiments also were made on the fluorination of unsubstituted acetamide. However, this compound could not be introduced from a saturator because of autocatalytic decomposition, or dropped in through a capillary on account of low liquid viscosity. Instead, it had to be dropped directly into the side arm of a T-reactor, placed on its side, from a buret without stopcocks, heated by a warm air jacket. The flow was controlled by measured reduced pressure applied at the top of the buret through a capillary. Under mild conditions, flow rate 0.035 mole/hour, reaction ratio 3:1:9 and temperature 218°, with balanced flow, cleavage was complete, presumably by carbonyl group attack, even before the hydrogen atoms of the methyl group had been replaced, and more than half the product was acetyl fluoride which on careful rectification gave pure CH_3COF, b.p. 7° at 500 mm., f.p. −84°, mol. wt. 62 (calcd. 62), identified as acetanilide, m.p. 112° (mixed 112°). Some oxidation to carbon dioxide was observed, due perhaps to dehydration of the amide, with subsequent action of fluorine on the water thus liberated. No products containing nitrogen were obtained, and the fate of the $\cdot NH_2$ radicals presumably liberated appears to be the same as in the direct fluorination or oxidation of ammonia, in which they are converted into elementary nitrogen. To confirm this, a run was made in which the exit gases rich in diluent helium were concentrated in nitrogen by adsorption on charcoal at low temperatures, followed by desorption. The final gas sample was shown by the mass spectrograph to be rich in nitrogen. Since unreacted acetamide could not be recovered without much decomposition, the theoretical value cannot be calculated accurately, but rough estimates based on the nature and amounts of the other products formed indicate a value approximating that actually observed. The overall evidence for this mechanism is therefore believed to be convincing. It is also of interest that trifluoroacetamide, when fluorinated under similar conditions at the ratio of 2:1:10 and 162°, yielded about 20% CF_3COF, and no products containing nitrogen.

The fluorination of the perfluoro alkyl nitriles CF_3CN and CF_3CF_2CN in the T-reactor was undertaken in the hope of preparing either by addition or subsequent pyrolysis the corresponding new half-adducts $CF_3CF{=}NF$ and $CF_3CF_2CF{=}NF$, homologs of $CF_2{=}NF$; and also in order to compare the results with the fluorination of acetonitrile reported earlier[5] from this Laboratory. The CF_3CN was fluorinated at the ratio of 3:1:9 and 275°, representing vigorous conditions, and yielded, in addition to cleavage products and a trace of $CF_2{=}NF$, C_2F_6, 55, and $CF_3CF_2NF_2$, 22 liq. vol. %, but neither the half-adduct nor any polymeric residue. Under mild conditions at the ratio of

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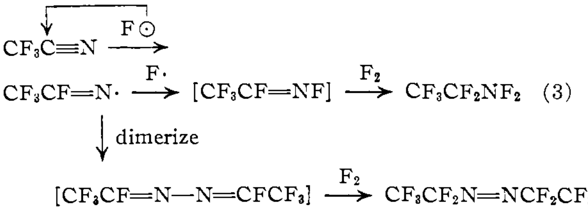
[4] E. A. Tyczkowski and L. A. Bigelow, THIS JOURNAL, **75**, 3523 (1953).

[5] J. A. Cuculo and L. A. Bigelow, *ibid.*, **74**, 710 (1952).

1:1:3 and 30–47°, there were formed, in addition to cleavage and transition, crude C_2F_6, 19, recovered CF_3CN, 47, and the new perfluoroazo compound $CF_3CF_2N{=}NCF_2CF_3$, b.p. 22°, f.p. −100°, 17 vol. %, but again no polymeric residue. In this mild reaction there was an induction period of several hours, followed by a sharp rise in the reactor temperature as the fluorination took place. It is estimated that during the initial period, about two-thirds of the sample mixed with fluorine passed through the reactor unchanged. No definite reason for this curious behavior is as yet apparent.

The fluorination of CF_3CF_2CN took place in a strictly similar manner. Under vigorous conditions at the ratio of 4:1:12 and 275° there were formed: crude $CF_4 + C_2F_6 + C_3F_8$ 31, pure C_3F_8 49, and the pure $CF_3CF_2CF_2NF_2$, b.p. 0°, f.p. −168°, 19 vol. %, not previously fully reported and nothing else. However, under mild conditions at the ratio of 1:1:3 and 54–65° there were formed essentially: recovered crude CF_3CF_2CN, 74, and the new pure $CF_3CF_2CF_2N{=}NCF_2CF_2CF_3$, b.p. 69° (26°, 160 mm.), f.p. −96°, 13 vol. %, and nothing else. In this case also the long induction period was observed, and almost three-quarters of the sample mixed with fluorine passed through the reactor unchanged.

The mechanisms involved in both cases may be represented by the illustrative scheme



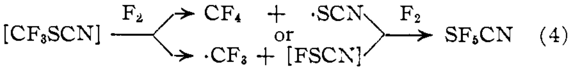
$$CF_3C{\equiv}N \xrightarrow{F\odot} CF_3CF{=}N\cdot \xrightarrow{F\cdot} [CF_3CF{=}NF] \xrightarrow{F_2} CF_3CF_2NF_2 \quad (3)$$

$$CF_3CF{=}N\cdot \xrightarrow{\text{dimerize}} [CF_3CF{=}N{-}N{=}CFCF_3] \xrightarrow{F_2} CF_3CF_2N{=}NCF_2CF_3$$

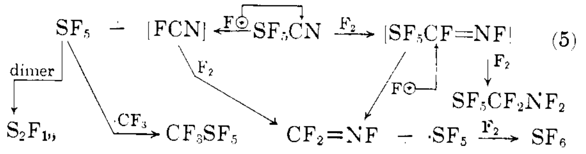
This mechanism does not predict polymerization, which is in accord with the facts; and it also accounts well for the observed lack of nitrogen balance, since the attack of fluorine upon the azo compounds might be expected to produce the corresponding fluorocarbons, which were actually formed, and elementary nitrogen, especially in the large T-reactor. It is quite different from the one proposed earlier for the fluorination of acetonitrile,[5] but it should be pointed out that the original radical obtained from an unsubstituted alkyl cyanide should be less stabilized by resonance and therefore more subject to polymerization, in accordance with the postulation made at that time.

It should be mentioned here that a number of pyrolyses over copper metal have been carried out in connection with this work. For instance, pure $(CF_3)_2NF$ at 515° gave the known azomethine $CF_2{=}NCF_3$, b.p. −33.5°, which we have found to freeze at −131°, in 64 vol. % yield. This compound was completely decomposed by cold dilute alkali and did not attack mercury, whereas its lower homolog $CF_2{=}NF$ is inert to cold dilute alkali and attacks mercury strongly. Also the pyrolysis of $CF_3CF_2NF_2$ and $CF_3CF_2CF_2NF_2$ readily yielded the corresponding nitriles, but none of the desired intermediates $CF_3CF{=}NF$ and $CF_3CF_2CF{=}NF$, as was also the case in the fluorination experiments described above.

Turning now to the interesting fluorination of methyl thiocyanate, CH_3SCN, runs have been made under both mild and relatively vigorous conditions. For instance, at the ratio of 4:1:100 and 90° (mild) about 38 vol. % of the total crude product was unchanged CH_3SCN. The remainder on rectification yielded: crude CF_4, 23; midcut, 48; and crude SF_5CN, b.p. −6 to −4°, 29 vol. %. On the other hand, at 6:1:90 and 95° (vigorous) no unchanged CH_3SCN was recovered, and finally there were formed: crude CF_4, 19; midcut, 63; and crude $SF_5CN + SF_5CF_2NF_2$, b.p. −6.5 to 8°, 17.5 vol. %. In the first case rectification of the high boiling product gave an 80% yield of pure SF_5CN which was a colorless liquid, b.p. −6°, f.p. −125°; while in the second case the high boiling product gave an 85% yield of apparently pure $SF_5CF_2NF_2$, which was also a colorless liquid, b.p. 9.5°, f.p. −153°. The large midcut obtained in these runs was a complex mixture, which even on prolonged treatment could be only partially resolved. According to the best possible estimate, the entire crude product from the second run described above contained roughly CF_4, 27; crude $CF_2{=}NF$, 12; SF_6, 35; CF_3SF_5, 2; SF_5CN, 7; $SF_5CF_2NF_2$, 15; and S_2F_{10}, 1 vol. % of the total in the order of their boiling points. There was considerable evidence to indicate that SF_5CN was fairly stable in the presence of fluorine, and may have served as the source for most of the other products formed; and it is also of interest that FCN, CF_3NF_2 and NF_3 did not appear to have been formed in this fluorination. While the reaction doubtless took place by several routes simultaneously the following speculative scheme appears to account well for the products actually isolated.



$$[CF_3SCN] \xrightarrow{F_2} \left\{ \begin{matrix} CF_4 + \cdot SCN \\ \text{or} \\ \cdot CF_3 + [FSCN] \end{matrix} \right\} \xrightarrow{F_2} SF_5CN \quad (4)$$



Experimental

The Fluorination of Dimethylformamide[6] (Large Scale Run).—The conventional apparatus used consisted essentially of a calibrated metal saturator, T-reactor, sodium fluoride tube and two collecting traps, one cooled by Dry Ice–acetone and the other by liquid air. In this representative run (selected from 3) helium at the rate of 0.308 mole/hour was passed through the saturator maintained at 86°, and carried the sample at the rate of 0.030 mole/hour into a T-tube where it was further diluted with 0.210 mole/hour of helium and then carried into the T-reactor maintained at an equilibrium temperature of 275°, where it met and reacted with fluorine at the rate of 0.360 mole/hour, diluted with helium at 0.194 mole/hour, such that the molar reaction ratio (F_2:sample:He) was 12:1:24. In this way a balanced flow was maintained in the two arms of the reactor, and the rise from base temperature was 20°. After 53 hours, the Dry Ice condensate (75 cc.) was rectified without stabilization; while the liquid air condensate consisting mostly of CF_4, CO_2 and COF_2 was discarded. The results of the rectification are presented later in Table I. The transitions were very small.

In the $(CF_3)_2NF$ fraction the infrared spectrum was the same at beginning, middle and end; but different from that

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(6) Donated by du Pont, redistilled, b.p. 153°.

TABLE I

THE RECTIFICATION OF FLUORINATED DIMETHYLFORMAMIDE

Compound	Boiling range, °C.	Molecular weight	Volume, cc.	Est. wt. % yield based on sample used
Forerun	< -50	93–147	3	. .
$(CF_3)_2NF$	-38	170–171	47	28
$(CF_3)_3N$	-6 to -5	220–221	10.5	4.9
$(CF_3)_2N-N(CF_3)_2$	-2(200 mm.)	300–304	10	3.4
Residue	. . . .	. . . .	4.5	. .

of $CF_3CF_2NF_2$. It was therefore concluded that essentially none of the latter isomer was present. Also, in a similar run, in which the fluorination ratio was 13.3:1 instead of 12:1, the yield of $(CF_3)_2NF$ rose to 38%.

The Fluorination of N-Methylformamide[7] **(Large Scale Run).**—The conventional apparatus was the same as before. In this representative run (selected from 6) helium at the rate of 0.345 mole/hour was passed through the saturator maintained at 118°, and carried the sample at the rate of 0.030 mole/hour into a T-tube where it was further diluted with 0.085 mole/hour of helium, and then carried into the T-reactor maintained at an equilibrium temperature of 275°, where it met and reacted with fluorine at the rate of 0.300 mole/hour, diluted with helium at 0.162 mole/hour, such that the molar ratio was 10:1:20 with a well balanced flow and rise from base temperature of 20° as before. After 38 hours, a Dry Ice condensate (23 cc.), and a liquid air condensate (89 cc.), stabilized through 5% NaOH (59 cc.) were obtained. The first and last of these were combined and the total crude product (82 cc.) then was rectified in the usual manner with the results shown below in Table II.

TABLE II

THE RECTIFICATION OF FLUORINATED N-METHYLFORMAMIDE

Fraction	Boiling range, °C.	Molecular weight	Liq. vol. % of total crude	Estimated composition
1	-129 to -125	83–87	35	CF_4
2	-105	86–91	6	Impure $CF_2{=}NF$, attacks Hg
3	-97	102–104	24	$CF_3NF_2 + COF_2$ does not attack Hg
4	-80 to -78	122–123	8.6	CF_3NF_2
5	-49 to -39	126–144	6	Transition
6	-39 to -38	166–170	11	$(CF_3)_2NF$
7	-34 to $+10$	177–291	8.6	

Fraction 4: Redistillation gave a central cut (4 cc.) of pure CF_3NF_2, b.p. −78°, f.p. −132°, mol. wt. 121 (calcd. 121).

Fraction 5: This portion attacked Hg, and may have contained $CF_3CF{=}NF$ (mol. wt. calcd. 133).

Fraction 6: Redistillation gave a central cut (7 cc.) of nearly pure $(CF_3)_2NF$, b.p. −38°, mol. wt. 170 (calcd. 171). However, although the infrared spectrum of this product corresponded mainly to that of pure $(CF_3)_2NF$, it did not fully exclude the presence of $CF_3N{=}NCF_3$ (known b.p. −32°, mol. wt. calcd. 166) as a contaminant.

Fraction 7: Redistillation yielded a small cut (2 cc.), b.p. 8 to 9° at 180 mm., mol. wt. 282–291, which may have been a pure chemical individual, but its exact nature has not as yet been determined.

The Fluorination of CF_3CN and CF_3CF_2CN.[8]—Inasmuch as these gases could not be metered successfully from the small commercial cylinders, they were first transferred to a glass displacement system using mineral oil. In a typical procedure CF_3CN was displaced through a calibrated flowmeter at the rate of 0.038 mole/hour, diluted with helium at 0.21 mole/hour, and conducted directly into the T-reactor maintained at an equilibrium temperature of 275°, where it met and reacted with fluorine at the rate of 0.114 mole/hour, diluted with helium at 0.133 mole/hour, such that the molar reaction ratio was 3:1:9. After 6 hours, 18 cc. of crude product was collected and rectified in the usual manner without stabilization. The results are shown in I, Table III, in which are collected the data from 4 selected runs out of 13 actually made.

TABLE III

THE RECTIFICATION OF FLUORINATED CF_3CN AND CF_3CF_2CN

<table>
<tr><th>Fraction</th><th>Boiling range, °C.</th><th>Molecular weight</th><th>Liq. vol. % of total crude</th><th>Estimated composition</th></tr>
<tr><td colspan="5">I. CF_3CN flow rate 0.038 mole/hour; ratio 3:1:9; temp. 275°; time 6 hr.; crude 18 cc.</td></tr>
<tr><td>1</td><td>-129 to -97</td><td>83–86</td><td>22</td><td>$CF_4 + CF_2{=}NF$(?)</td></tr>
<tr><td>2</td><td>-80 to -79</td><td>133–138</td><td>55</td><td>C_2F_6</td></tr>
<tr><td>3</td><td>-36</td><td>170–172</td><td>22</td><td>$CF_3CF_2NF_2$</td></tr>
<tr><td colspan="5">II. CF_3CN flow rate 0.07 mole/hour; ratio 1:1:3; temp. 30–47°; time 9.7 hr.; crude 47 cc.</td></tr>
<tr><td>1</td><td>-109 to -81</td><td>83–100</td><td>10.6</td><td>Forerun</td></tr>
<tr><td>2</td><td>-80 to -78</td><td>119–103</td><td>19</td><td>$C_2F_6 + CF_3CN$</td></tr>
<tr><td>3</td><td>-71 to -69</td><td>99–95</td><td>47</td><td>Crude CF_3CN</td></tr>
<tr><td>4</td><td>-44 to 0</td><td>138–180</td><td>6</td><td>Transition</td></tr>
<tr><td>5</td><td>22</td><td>266–269</td><td>17</td><td>$C_2F_5N{=}NC_2F_5$</td></tr>
<tr><td colspan="5">III. C_2F_5CN flow rate 0.06 mole/hour; ratio 4:1:12; temp. 275°; time 14 hr.; crude 57 cc.</td></tr>
<tr><td>1</td><td>-129 to -91</td><td>78–94</td><td>7</td><td>Crude CF_4</td></tr>
<tr><td>2</td><td>-88 to -44</td><td>102–155</td><td>12</td><td>C_2F_6 + trans.</td></tr>
<tr><td>3</td><td>-44 to -40</td><td>164–180</td><td>12</td><td>Crude C_3F_8</td></tr>
<tr><td>4</td><td>-40 to -38</td><td>183–189</td><td>49</td><td>C_3F_8</td></tr>
<tr><td>5</td><td>-1 to 0</td><td>216–221</td><td>19</td><td>$CF_3CF_2CF_2NF_2$</td></tr>
<tr><td colspan="5">IV. C_2F_5CN flow rate 0.06 mole/hour; ratio 1:1:3; temp. 54–65°; time 7 hr.; crude 38 cc.</td></tr>
<tr><td>1</td><td>-128 to -56</td><td>61–94</td><td>5</td><td>Forerun</td></tr>
<tr><td>2</td><td>-37 to -32</td><td>142–152</td><td>74</td><td>Crude C_2F_5CN</td></tr>
<tr><td>3</td><td>-29 to 0</td><td>155–187</td><td>5</td><td>Transition</td></tr>
<tr><td>4</td><td>26 (160 mm.)</td><td>362</td><td>13</td><td>$C_3F_7N{=}NC_3F_7$</td></tr>
</table>

Fraction I, 3: This portion was combined with similar material (8.5 cc. in all) and redistilled, yielding a central cut, b.p. −36°, which became a glass near −171°, known b.p. −38°, f.p. −183°.[5]

Fraction II, 5: This material (8 cc.) was redistilled, yielding a central cut (3 cc.) of pure, pale yellow $C_2F_5N{=}NC_2F_5$, b.p. 22°, f.p. −100° (sharp), mol. wt. 266 (calcd. 266).

The n.m.r. spectrum consists only of two fluorine bands at +7.7 and +37.2 p.p.m. from CF_3COOH, corresponding both in position and relative intensity ratios to the well-known values for the perfluoroethyl groups contained in the proposed structure.

Anal. Calcd. for $C_4F_{10}N_2$: N, 10.5 Found: N, 10.8.

Fraction III, 5: Similar material on redistillation yielded a central cut (4 cc.) of pure $CF_3CF_2CF_2NF_2$, b.p. 0°, f.p. −168° (sharp), mol. wt. 221 (calcd. 221).

The n.m.r. spectrum fits the proposed structure and corresponds with a minor exception to that previously reported by Muller, *et al.*[9] It should be noted, however, that these investigators have not as yet recorded the physical properties of the sample which they measured or given any account of how this material was either obtained or prepared.

Fraction IV, 4: This sample (5 cc.) was redistilled yielding a central cut (4 cc.) of pure $CF_3CF_2CF_2N{=}NCF_2CF_2CF_3$, b.p. 69° (1 atm.), f.p. −96° (sharp), mol. wt. (crude) 362 (calcd. 366).

The n.m.r. spectrum consists of three main bands at +5.8, +33.6 and +52.8 p.p.m. from CF_3COOH corresponding to the well-known values for the perfluoro-*n*-propyl

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(7) Supplied by Distillation Products, Inc., redistilled, b.p. 197–198°.

(8) Both supplied by Peninsular Chemicals, Gainesville, Fla., redistilled, b.p. −68° and −37°, respectively.

(9) N. Muller, P. Lauterbur and G. Svatos, THIS JOURNAL, **79**, 1807 (1957).

groups present in the proposed structure. Certain minor bands indicate relatively small amounts of impurities in this material.

The mild fluorinations (II and IV) required a long induction period before the reaction set in. In II, for example, approximately two thirds of the sample although mixed with fluorine passed through the reactor unchanged before a significant rise in temperature was observed.

Pyrolysis of $(CF_3)_2NF$ (Specimen Procedure).—The pyrolyzer consisted of a 32" section of electrically heated 1" brass pipe packed with copper shot, and equipped at each end with 0.5" straight unions soldered in. One end was connected to the sample source, and the other to a set of receiving traps, while a 6" length of $^3/_8$" copper tubing closed at one end was soldered perpendicularly into the body of the pyrolyzer at its midpoint to serve as a thermometer well. In preparation, clean copper shot, moist with methanol, was placed in the unit, which then was flushed with deoxygenated helium at 150° for four hours. After this the unit was thoroughly fluorinated out at 250° and again flushed with helium. Great care was taken to prevent the introduction of air or moisture as far as possible at all times. In operation, pure $(CF_3)_2NF$ (9 cc. of liquid corresponding to 1800 cc. of gas at 1 atm.) was displaced at the rate of 1.0 liter/hour, diluted with He at 1.0 liter/hour, and passed through the pyrolyzer maintained at 515°. It was followed by helium at 1.0 liter/hour for 2 hours to sweep all the products into the condensing traps cooled by liquid oxygen. The pass time was approximately 15 minutes, and the crude product amounted to 7 cc. of liquid, which was then rectified: Forerun ($COF_2 + CO_2$), b.p. −79 to −56°, mol. wt. 51–66, 36 vol. %; and $CF_2{=}N{-}CF_3$, b.p. −33 to −32° mol. wt. 130–131, 64 vol. %. Accumulated product refractionated yielded pure $CF_2{=}N{-}CF_3$, b.p. −33.5°, f.p. −131° (sharp), mol. wt. 133 (calcd. 133).

The Fluorination of Methyl Thiocyanate.—This material, obtained from Distillation Products, Inc., was fluorinated in the packed concentric ring reactor previously described.[10] The sample was carried in on nitrogen from a calibrated glass saturator consisting essentially of an electrically heated three-necked flask partially filled with porous chips covered with the liquid sample, and equipped with the necessary thermometer and connections. In all, some half-dozen runs were made, of which two will be detailed. In each, N_2 at the rate of 3.35 liters/hour was passed into the saturator maintained at 104°, and carried the sample at 0.0274 mole/hour directly into the central ring of the reactor, while undiluted fluorine was admitted to the outer ring, and the remainder of the diluent N_2 to the intermediate ring to serve as a barrier.

Run I (Mild).—The CH_3SCN met and reacted with fluorine under conditions such that the molar reaction ratio (F_2:sample:N_2) was 4:1:100, and temperature 90° (rise from base 5°). After 25.5 hours 15 cc. of unreacted sample was recovered, and 24 cc. of crude volatile product resulted which then was rectified. There were formed, expressed in liquid volume per cent. of the total crude volatile condensate: crude CF_4, 23; midcut (b.p. −105 to −5°, mol. wt. 90–150), 48; and crude SF_5CN (b.p. −6 to 4°, mol. wt. 153–157), 29. The last fraction was redistilled, and 80% of it recovered as pure SF_5CN, b.p. −6°, f.p. −125°, mol. wt. 153 (calcd. 153).

The n.m.r. spectrum consists of two fluorine bands at −126.2 and −28.6 p.p.m. from CF_3COOH. The former can be resolved into a quadruplet and the latter into a triplet, while the area of the first band is two-thirds that of the second. This spectrum indicates the presence of a single non-fluorine substituent on an SF_5^- radical, and also suggests that this substituent replaces one of the four planar fluorines attached to the SF_6 octahedron. The infrared spectrum does not show a band at the usual $-C{\equiv}N$ position, but this does not rule out the proposed structure, since this band is not strong in compounds containing oxygen substituents near the nitrile group; and sulfur may well have the same effect. The mass spectrum gives ions attributed to SF_5CN^+, SF_4CN^+, SF_5^+, SF_3CN^+, SF_3^+, SF_2^+, SFN^+, SF^+ and SN^+. From this it appears that the product consisted mainly of SF_5CN, possibly contaminated with a little SF_5NC unless some rearrangement occurred during the observations, which would be easily possible under the circumstances. There was also evidence of the presence of fluorocarbon impurities in this product, but these could have been greatly concentrated by fractionation during the sampling.

Run II (Vigorous).—The CH_3SCN met and reacted with fluorine under conditions such that the molar reaction ratio (F_2:sample:N_2) was 6:1:90, and temperature 95° (rise from base 9 to 10°). After 42 hours 51.5 cc. of crude volatile material was produced which then was rectified. There were formed: crude CF_4, 19.4; midcut (rapidly removed), 63; crude $SF_5CN + SF_5CF_2NF_2$ (b.p. −6.5 to 8°, mol. wt. 162–254), 17.5. The last fraction was redistilled twice and approximately 85% of it recovered as apparently pure $SF_5CF_2NF_2$, b.p. 9.5°, f.p. −153°, mol. wt. 229 (calcd. 229).

This sample appeared to change slowly on standing, even after further redistillation. After some time the n.m.r. spectrum was measured and was not then consistent with the proposed structure, nor did it indicate any related structure which could be suggested. The complete resolution of this problem must await further study.

The large midcut obtained in every run was a highly complex mixture, very difficult to separate. It was subjected to redistillations, stabilizations by alkali, recombinations and still further rectifications, which even then were not entirely successful. For example, from the midcut in run II above there was obtained a fraction, b.p. −99 to −93°, mol. wt. 81–83, which attacked mercury strongly, and which almost certainly consisted largely of $CF_2{=}NF$ (known b.p. −101°, mol. wt. calcd. 83); and this was followed later by a portion (after stabilization and distilled in part at 2.1 atm.), b.p. −72 to −61° (corrected to 1 atm.) mol. wt. 136–150, which was crude SF_6 (sublimes at −64°, mol. wt. calcd. 146). Then a small fraction was obtained, b.p. −18 to −5°, mol. wt. 189–196, which was shown by its infrared spectrum to consist almost entirely of CF_3SF_5 (known b.p. −20°, mol. wt. calcd. 196); and this was followed by a portion, b.p. −5 to −3°, mol. wt. 162–166, which seemed to consist largely of SF_5CN, b.p. −6°, mol. wt. calcd. 152. In addition to all of these the midcut also contained a small amount of $SF_5CF_2NF_2$ described above; and a very small residual portion boiling above 15°, mol. wt. 254, which was undoubtedly S_2F_{10} (known b.p. 25°, mol. wt. calcd. 254). According to the best estimate, the fluorination product from CH_3SCN in run II contained roughly (in vol. %): CF_4, 27; crude $CF_2{=}NF$, 12; SF_6, 35; CF_3SF_5, 2; SF_5CN, 7; $SF_5CF_2NF_2$, 15; and S_2F_{10}, 1.

It should be noted here that precise quantitative analyses of compounds containing C, F and N, with or without S, and no H, are not easy to perform. The new compounds listed above were analyzed in three different laboratories and by different methods. Good checks sometimes could be obtained by the same operator using the same method, but the figures obtained with one exception as noted, agreed only approximately either with the calculated values or with each other, and are therefore considered unreliable.[11]

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(10) J. A. Gervasi, M. Brown and L. A. Bigelow, THIS JOURNAL, **78**, 1679 (1956).

(11) At the Editor's request, we cite an illustrative example: Pure SF_5CN gave %F by Lab A, method 1, 58.6, 58.7; method 2, 60.0, 60.4; Lab B, 78.2; Lab C, 66.0 as against the calcd. value 62.1.