atom solvation, not much less active as a catalyst than trifluoroacetic acid.

An alternate explanation, which cannot be discounted, can be offered for the difference in rate response of the aromatic chlorination and dichloride dissociation reactions to the replacement of trifluoroacetic acid catalyst by its mixed dimer with acetic acid. Again it is assumed that the primary solvation sites in the activated complexes are the negative ends of the dipoles and that the mixed dimer is less suited for this purpose than is trifluoroacetic acid. The magnitude of the effect of change in the acid may then be related to the degree to which polarization (in one case of an I–Cl bond and in the other of a Cl–Cl bond) occurs in the activation process. That is, the extent to which the changes in solvating power of the catalyst (as it is converted to mixed dimer) is reflected in reaction rate will depend on the extent to which development of negative charge takes place when activation occurs. If this argument is correct, the activated complex for aromatic chlorination in carbon tetrachloride must be substantially more polar than that for dichloride dissociation.

Whether the magnitude of the acetic acid effect is related to the degree to which polarization accompanies activation or to the degree to which solvation of an electropositive center controls the energetics of activation, it seems reasonable that trichloroacetic acid should be less inhibitory than acetic acid (see Table IV and V). The stronger acid, which itself has some catalytic activity, should not reduce the anion solvating power of trifluoroacetic acid through mixed dimer formation as much as should acetic acid. It has been observed previously that combinations of acids may be less effective as catalysts for reactions in non-polar media than one would predict on the basis of their individual activities, in particular when the reactivities of the two compounds are far apart.[15]

**Acknowledgment.**—The authors are indebted to the National Science Foundation for a grant in support of this research.

[15] J. N. Brönsted and R. P. Bell, THIS JOURNAL, **53**, 2478 (1931).

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF FLORIDA]

# Fluorocarbon Nitrogen Compounds. VII.[1] The Indirect Fluorination of Some Fluorocarbon Nitrogen Derivatives[2]

BY JOHN A. YOUNG, WILLIAM S. DURRELL AND RICHARD D. DRESDNER

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The indirect fluorination of some fluorocarbon nitrogen compounds has been investigated and reactions of the following functional groups have been determined under mild conditions: $—N{=}C<$, $N{\equiv}C—$, $c—(—N{=}C<)_3$, $>N—H$, $>NCOF$, $—N{=}C{=}O$, $—NHCOF$, $—CONH_2$ and $—CONHCO—$. Fluorocarbon N–F compounds can be synthesized in certain cases by the action of silver difluoride on carbon–nitrogen unsaturation, by replacement of amine hydrogen or by cleavage of an acyl group from nitrogen. Rearrangement and coupling of the free radical intermediates are competitive with N–F bond formation, coupling becoming more important with progressively milder conditions. Volatile fluorocarbon isocyanates can be conveniently prepared from the corresponding amides by reaction with $AgF_2$, and fluorocarbon azoalkanes, $R_FCF_2N{=}NCF_2R_F$, from nitriles by use of the same reagent. Similarity of the isocyanate synthesis to the Hofman and Curtius reactions is discussed.

Although the fluorination of many nitrogen compounds by various methods has been rather extensively studied,[3] little has been done with fluorocarbon nitrogen derivatives, which, by virtue of their lack of hydrogen external to the functional group, might be expected to exhibit cleaner, less complex behavior toward fluorinating agents. This paper describes the reaction of three types of functional groups—carbon–nitrogen unsaturation, amine or amide hydrogen and carbonyl—when fluorocarbon compounds containing these groups, alone or in combination, are treated with silver difluoride under mild conditions.

It has previously been shown[4,5] that fluorination of carbon–nitrogen unsaturation in fluorocarbon derivatives proceeds *via* a nitrogen-containing free radical. Extension to functional groups other than unsaturation, as described in the present work, shows that this generalization holds true. In every case the products may be adequately explained by postulating initial formation of an intermediate carrying an unpaired electron on nitrogen, this intermediate then reacting by coupling, rearrangement or saturation with fluorine.

The primary intermediate may be formed in any of several ways, depending on the structure of the reactant. If carbon–nitrogen unsaturation is present, fluorine attacks the carbon atom.

$$CF_3N{=}CF_2 \longrightarrow (CF_3)_2N\cdot \qquad (1)$$

$$R_FC{\equiv}N \longrightarrow R_FCF{=}N\cdot \qquad (2)$$

If an N–acyl bond is present, the acyl group may be eliminated as an acid fluoride.

$$(CF_3)_2NCOF \longrightarrow (CF_3)_2N\cdot + COF_2 \qquad (3)$$

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[1] For the preceding paper in this series, see J. A. Young, S. N. Tsoukalas and R. D. Dresdner, THIS JOURNAL, **82**, 396 (1960).

[2] Presented in part at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959. This work was supported by the Office of Naval Research and by the Office of Ordnance Research; reproduction in whole or in part is permitted for any purposes of the U. S. Government.

[3] (a) O. Ruff and H. Giese, *Ber.*, **69**, 598 (1936); (b) O. Ruff and W. Willenburg, *ibid.*, **73**, 724 (1940); (c) W. Huckel, *C. A.*, **44**, 4359 (1950); (d) G. E. Coates, J. Harris and T. Sutcliffe, *J. Chem. Soc.*, 2762 (1951); (e) F. Nerdel, *Naturwiss.*, **39**, 209 (1952); (f) J. Cuculo and L. A. Bigelow, THIS JOURNAL, **74**, 710 (1952); (g) F. P. Avonda and L. A. Bigelow, *ibid.*, **78**, 2978 (1956).

[4] J. A. Young, W. S. Durrell and R. D. Dresdner, *ibid.*, **81**, 1587 (1959).

[5] J. H. Attaway and L. A. Bigelow, *ibid.*, **81**, 3599 (1959).

If an N–H bond is present, hydrogen is abstracted

$$(CF_3)_2NH \longrightarrow (CF_3)_2N\cdot + HF \qquad (4)$$

The direction of further reaction depends greatly upon reaction conditions. In a highly energetic environment, *i.e.*, large excess of fluorinating agent, good contact, and high temperatures, fluorine pickup by the free radical is favored.

$$(CF_3)_2N\cdot + AgF_2 \longrightarrow (CF_3)_2NF + AgF \qquad (5)$$

A coupling reaction, as shown in reaction 6, is always competitive with reaction 5 and is often predominant, moderation of reaction conditions favoring coupling.

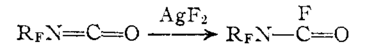
$$2(CF_3)_2N\cdot \longrightarrow (CF_3)_2N{-}N(CF_3)_2 \qquad (6)$$

The effect of changing reaction conditions on the competition between N–F or C–F bond formation and coupling can be seen in other types of fluorination as well. Thus, in the liquid phase fluorination of chlorofluoro olefins, Miller[6] found that additive dimerization increased with decreasing temperature, at the expense of simple addition of fluorine. Bigelow[5] found a complete change in the nature of the direct fluorination products of trifluoroacetonitrile, $CF_3CF_2NF_2$ resulting at high temperatures and fluorine concentrations, $CF_3CF_2N{=}NCF_2CF_3$ at low. Dresdner,[7] in a study of the reaction of $NF_3$ with $CF_3CF{=}CF_2$, found that at 520° a large part of the olefin was converted to $C_3F_8$; at 320° little $C_3F_8$ was formed and products resulting from coupling of perfluoroisopropyl radicals predominated. In the electrochemical fluorination process similar results have been observed. The electrolysis of pyridine in HF at 5.0–5.5 volts gave a fair yield of c-$(CF_2)_5NF$ and a small amount of perfluoro-1,1-dipiperidyl[8]; if the impressed voltage is lowered by 0.5 volt, the yield of fluoramine decreases sharply and that of the coupled product increases substantially.[9] It should be possible, therefore, to control the nature of the products to some extent by selection of proper conditions.

In the illustrations given in reactions 1, 3 and 4, the same perfluorodimethylamino free radical is formed from $CF_3N{=}CF_2$, $(CF_3)_2NCOF$, and $(CF_3)_2NH$, although the mode of formation differs in each case. The final products should then be identical, and this fact has been found to be true, all three of these compounds giving various relative amounts of $(CF_3)_2NF$ and $(CF_3)_2NN(CF_3)_2$, depending on the exact conditions used.

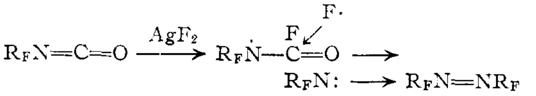
It was thought that some measure of the relative preference for each of these modes of reaction—attack at an unsaturated carbon, attack at carbonyl carbon and abstraction of hydrogen from N–H—could be acquired from the behavior of compounds which contained more than one type of functional group. For this purpose the compounds $C_2F_5N{=}C{=}O$, $CF_3CONH_2$, $C_2F_5NHCOF$ and $(CF_3CO)_2NH$ were studied.

In the case of the isocyanate, it would be expected that fluorine would attack the carbonyl carbon quite readily to give the structure



$$R_FN{=}C{=}O \xrightarrow{AgF_2} R_FN{-}\overset{F}{C}{=}O \qquad (7)$$

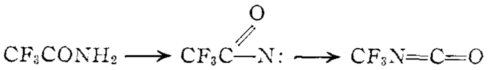
This intermediate could then undergo either loss of the carbonyl group or reaction at the nitrogen free radical by coupling or fluorine attack. The identity of the products, $COF_2$ and $C_2F_5N{=}NC_2F_5$, showed that the first of these processes had occurred. Since neither $R_FNF_2$ nor $(R_FNF)_2$ was detected, it appears that no fluorine attack on nitrogen took place, and that the probable intermediate was the species $R_FN$:



$$R_FN{=}C{=}O \xrightarrow{AgF_2} R_F\dot{N}{-}\overset{F\cdot}{\overset{F\swarrow}{C}}{=}O \longrightarrow R_FN\!: \longrightarrow R_FN{=}NR_F \qquad (8)$$

A somewhat similar six-electron intermediate was found in the case of trifluoroacetamide. This compound reacted so vigorously with $AgF_2$ that it was necessary to moderate the reaction by suspending the amide in a inert solvent and adding the silver difluoride slowly. Under these conditions some $CF_3COF$ and $CF_3CN$ were formed, but the main product, obtained in 58% yield, was the isocyanate $CF_3N{=}C{=}O$.

Formation of the isocyanate can be accounted for by assuming that the initial reaction was hydrogen abstraction. Loss of the second hydrogen, either by stepwise abstraction or by fluorination and concerted loss of HF, would lead to an electron-deficient intermediate identical with that postulated for the Hofmann and Curtius reactions. Subsequent internal rearrangement of this intermediate, as in those reactions, would give the isocyanate

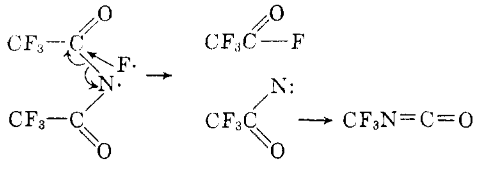


$$CF_3CONH_2 \longrightarrow CF_3\overset{O}{C}{-}N\!: \longrightarrow CF_3N{=}C{=}O \qquad (9)$$

It is probable that the large yield of isocyanate was due at least in part to its volatility, since isocyanates react with $AgF_2$, as shown earlier, to form $COF_2$ and azoalkanes. Some indication of $CF_3N{=}NCF_3$ was found, but the greater part of the isocyanate escaped unchanged. Conditions could probably be varied to produce either the isocyanate or the azoalkane as the principal product. The reaction constitutes a convenient synthesis of those fluorocarbon isocyanates which are not easily accessible *via* the Curtius reaction because of the low boiling points of the corresponding acid chlorides.

Reaction of $(CF_3CO)_2NH$ with $AgF_2$ in the same manner as that of the amide led to cleavage of the imide linkage and formation of $CF_3COF$ and $CF_3NCO$. This result shed some light on the mechanism of the previous reaction, since in the case of the imide, if the first step is assumed to be hydrogen abstraction, no plausible further reaction on nitrogen can be written which could lead to the isocyanate. It is likely, therefore, that the second step was attack of fluorine on the carbonyl carbon, as shown in reaction 11.

$$(CF_3CO)_2NH \xrightarrow{AgF_2} (CF_3CO)_2N\cdot \qquad (10)$$



(11)

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(6) W. T. Miller and S. D. Koch, THIS JOURNAL, **69**, 3084 (1957).

(7) R. D. Dresdner, F. N. Tlumac and J. A. Young, paper V in this series, in preparation.

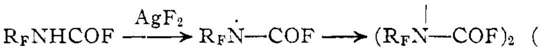
(8) T. C. Simmons, R. B. Beck, *et al.*, THIS JOURNAL, **79**, 3429 (1957).

(9) Unpublished work of the authors.

Subsequently, or simultaneously, homolysis of the carbon–nitrogen bond occurred and the $\mathrm{R_F}$-CON: intermediate was formed, which rearranged to the isocyanate.

Since this mechanism necessitates preferential attack of fluorine at carbon and not at the nitrogen free radical, its plausibility in this case supports the contention that a similar sequence is followed in the cases of both the nitrile and the isocyanate, and that a nitrogen diradical, or six electron intermediate, is present in all three cases.[10] It has been alleged[11] that in the related Hofmann and Curtius reactions, the six-electron nitrogen structure is not a true intermediate, and that the rearrangement occurs *via* a concerted elimination of halide ion or nitrogen, respectively. The present work would seem to indicate that at least in the Curtius reaction, where conditions are more nearly similar, the possibility of such an intermediate cannot be completely disregarded.

In fluorination of the compound $\mathrm{C_2F_5NHCOF}$ (made by addition of HF to $\mathrm{C_2F_5N{=}C{=}O}$), the NH group was found to be much less reactive toward AgF than the others studied, no reaction occurring at 70°. At 100° reaction took place to a moderate extent, with formation of small amounts of the azoalkane and also of a second compound which may have been the coupled bis-carbamyl fluoride.



$$\mathrm{R_FNHCOF} \xrightarrow{\mathrm{AgF_2}} \mathrm{R_F\dot{N}{-}COF} \longrightarrow (\mathrm{R_F\overset{|}{N}{-}COF})_2 \quad (12)$$

At 150°, with a shorter reaction time only the azoalkane was found, with no coupled carbamyl fluoride. The last result may have been due to loss of HF from the carbamyl fluoride before fluorination occurred, so that the effective reactant was the isocyanate rather than the carbamyl fluoride.

Conclusions concerning the relative probability of occurrence of each of the three modes of reaction (reactions 1, 3 and 4), where more than one is possible, must be very tentative since the data are drawn from only four compounds. Reasoning from the high reactivity of $\mathrm{CF_3CONH_2}$ and $\mathrm{(CF_3CO)_2NH}$, from the formation of a possible N–N coupled product in the case of $\mathrm{C_2F_5NHCOF}$, and from the fact that $\mathrm{CF_3N{=}C{=}O}$ was largely unaffected by reaction conditions which attacked $\mathrm{CF_3CONH_2}$, it would appear that abstraction of hydrogen from N–H is favored over fluorine attack at either carbonyl or unsaturated carbon.

Reactivity of the individual functional groups is of course influenced by other structure in the molecule. Incorporation of the carbon–nitrogen double bond in a stabilized structure such as the triazine ring greatly decreased its reactivity toward fluorinating agents. Thus, although several metal fluorides were found to catalyze trimerization to triazines (see Table I), the triazine ring so formed gave little further reaction with $\mathrm{AgF_2}$ at temperatures up to 150°. The small amount of reaction actually taking place did not fluorinate the ring but cleaved it, and indications of such fragments as $\mathrm{CF_4}$ and possibly $\mathrm{CF_3NF_2}$ were found.

TABLE I

THE TRIMERIZATION OF $\mathrm{CF_3CN}$

| Catalyst | Catalyst: nitrile ratio (moles) | Conditions Hr. | Conditions $T$, °C. | Yield of triazine, % |
|---|---|---|---|---|
| None[a] | 0 | 16 | 300 | 25 |
| $\mathrm{HgF_2}$ | 2.3 | 20 | 150–200 | 40 |
| AgF | 0.7 | 44 | 100 | 47–64 |
| $\mathrm{AgF_2}$ | 3.0 | 48 | 100 | 20[b] |

[a] W. L. Reilly and H. C. Brown, *J. Org. Chem.*, **22**, 698 (1957). [b] The main product in this case was the azoalkane.

## Experimental

**Reaction of $\mathrm{CF_3CN}$ with $\mathrm{HgF_2}$.**—Twenty-five grams of $\mathrm{CF_3CN}$ (0.26 mole) and 146 g. of $\mathrm{HgF_2}$ (0.61 mole) were rocked in a stainless steel autoclave at 150–200° for 20 hr. Fractionation of the 25 g. of crude product gave only two products: 14 g. of unreacted $\mathrm{CF_3CN}$, mol. wt. 96–97, and 10 g. of material, b.p. 93.5–95°, $n^{25}\mathrm{D}$ 1.3200, mol. wt. 290. Known values[11] for $\mathrm{(CF_3CN)_3}$ are b.p. 95°, $n^{25}\mathrm{D}$ 1.3161, mol. wt. 285. Comparison of an infrared spectrum with that of known $\mathrm{(CF_3CN)_3}$ confirmed the identification. The trimerization conversion was 40% of theory.

**Reaction of $\mathrm{CF_3CN}$ with AgF.**—Thirty grams of $\mathrm{CF_3CN}$ (0.31 mole) and 30 g. of AgF (0.02 mole) were sealed in an autoclave and rocked at 100° for 44 hours. Fractionation of the 22 g. of crude product (some was evidently lost by leakage) gave 8 g. of unreacted $\mathrm{CF_3CN}$, mol. wt. 91–95. The remainder was all triazine, b.p. 95–96°, $n^{29}\mathrm{D}$ 1.3187. This amounts to 47% trimerization based on the original 30 g., or 64% based on the total amount recovered.

**Reaction of $\mathrm{(CNF)_3}$ with $\mathrm{AgF_2}$.**—Fourteen grams of $\mathrm{(CNF)_3}$ (0.1 mole), made by a modification of Bigelow's method,[12] and 100 g. of $\mathrm{AgF_2}$ (0.69 mole) were loaded into an autoclave and rocked at 50°. After 18 hours, a series of molecular weights were taken, the observed values being 118, 131, 132, 133 (mol. wt. $\mathrm{(CNF)_3}$ 135). The same charge of triazine was returned to the bomb and rocked at 150° for 10 hours. Fractionation of the resulting product (10 g.) gave 2 g. overhead through an ice-water cooled condenser. The remainder, 8 g., 57% recovery, was unreacted triazine, b.p. 70–73°, mol. wt. 135. An infrared spectrum of the more volatile product showed lines ascribed to $\mathrm{CF_4}$ (7.8 $\mu$) and $\mathrm{CF_3NF_2}$ (9.7, 10.3, 14.1 $\mu$).

**Reaction of $\mathrm{(CF_3CN)_3}$ with $\mathrm{AgF_2}$.**—Thirteen grams (0.05 mole) of $\mathrm{(CF_3CN)_3}$ and 50 g. of $\mathrm{AgF_2}$ (0.34 mole) were rocked in an autoclave for 76 hours at 100°. After this time 3 g. of volatile material was obtained, mol. wt. 83–88, which on infrared examination proved to be mainly $\mathrm{CF_4}$. The rest of the triazine (77%) was recovered unchanged.

**Reaction of $\mathrm{CF_3CN}$ with $\mathrm{AgF_2}$ at 100°.**—Twenty-five grams of $\mathrm{CF_3CN}$ (0.26 mole) and 100 g. of $\mathrm{AgF_2}$ (0.68 mole) were rocked at 100° for 48 hours. Fractionation of the 31 g. of crude product gave 3 g. overhead through a Dry Ice-cooled condenser and 2 g., b.p. −59 to +20°, mol. wt. over this range 95–114, both fractions consisting of $\mathrm{CF_3CN}$, $\mathrm{CF_4}$ and $\mathrm{C_2F_6}$, according to infrared evidence.

There followed 20 g. of $\mathrm{C_2F_5N{=}NC_2F_5}$, b.p. 20–23°, mol. wt. 264 (calcd. 266). A center cut, b.p. 22°, was shown chromatographically to be >99% pure. An infrared spectrum was identical with that for $\mathrm{C_2F_5N{=}NC_2F_5}$, furnished by Dr. L. A. Bigelow, with peaks as follows: 7.33, 7.43(m), 8.05(vs), 8.48(vs), 9.33(vs), 13.25, 14.12, 14.80 $\mu$ (all weak). Yield of $\mathrm{(C_2F_5)_2N_2}$, based on unrecovered nitrile, was 68% of theory.

The residue, 5 g., consisted mainly of $\mathrm{(CF_3CN)_3}$, plus traces of $\mathrm{CF_3COOH}$.

**Reaction of $\mathrm{C_3F_7CN}$ with $\mathrm{AgF_2}$.**—Thirty five grams of $\mathrm{C_3F_7CN}$ (0.18 mole) and 100 g. of $\mathrm{AgF_2}$ (0.68 mole) were loaded into an autoclave and rocked at 100° for 24 hours. The reaction product was then pumped out of the bomb *in vacuo* and fractionated to give 20 g. of yellow liquid b.p. 45–47° (60 mm.). A chromatograph of a heart cut b.p. 47° (60 mm.), $n^{28}\mathrm{D}$ 1.2730, $d^{28}{}_4$ 1.672, showed 98%

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(10) With $\mathrm{CF_3CN}$, the sequence would be $\mathrm{{-}CF{=}N\cdot \rightarrow {-}CF_2N \rightarrow {-}CF_2N{=}NCF_2{-}}$, rather than $\mathrm{{-}CF{=}N\cdot \rightarrow {-}CF{=}N{-}N{=}CF{\equiv} \rightarrow {-}CF_2N{=}NCF_2{-}}$, as postulated by Bigelow.)

(11) Jack Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, New York, 1956, p. 317.

(12) A. F. Maxwell, J. S. Fry and L. A. Bigelow, THIS JOURNAL, **80**, 548 (1958).

purity. An n.m.r. spectrum showed peaks at $\delta = 5.6$ ($CF_3$), 32.7 ($\alpha$-$CF_2$), and 48.7, 50.3 ($\beta$- and $\gamma$-$CF_2$), while infrared peaks appeared at 7.35(s), 7.65(s), 7.75–8.50(s), 8.60(s), 8.65–8.80 (doublet, s), 11.30(s), 13.20–13.50(triplet, m), 13.75(m), 14.0(m) $\mu$. The yield of $(C_4F_9)_2N_2$ was 57%. The n.m.r. spectrum was taken on a Varian Associates instrument using a 40 mc. proble. The $\delta$-values are relative to $CF_3COOH$.

*Anal.* Calcd. for $C_8F_{18}N_2$: C, 20.6; F, 73.4; N, 5.94; *MR*D, 47.1. Found: C, 19.6; F, 71.86; N, 5.81; *MR*D, 47.8.

**Reaction of $(CF_3)_2NH$ with $AgF_2$.**—Twenty-five grams of $(CF_3)_2NH$ (0.16 mole) and 50 g. of $AgF_2$ (0.35 mole) were rocked in an autoclave for 15 hours at 50°. The volatile contents were then vacuum-transferred into NaF to remove HF and fractionated, giving 3 g. $(CF_3)_2NF$, b.p. −34 to −20°, mol. wt. 167–171; 6 g. of $(CF_3)_2NH$, b.p. −10 to −2, mol. wt. 153–158; and 11 g. of $(CF_3)_2NN(CF_3)_2$, b.p. 31°, mol. wt. 304, chromatographic purity 99%. Infrared spectra checked very well with those of the known compounds and the amounts obtained represent yields of 11 and 44%, respectively, for $(CF_3)_2NF$ and $(CF_3)_2NN(CF_3)_2$.

**Reaction of $(CF_3)_2NCOF$ with $AgF_2$.**—Twenty grams of $(CF_3)_2NCOF$ (0.10 mole) and 30 g. of $AgF_2$ (0.21 mole) were rocked in an autoclave at 100°. After 6 hours the pressure rise ceased, but heating was continued for an additional 12 hours. Fractionation of the 23 g. of volatile products gave 57 g. of $COF_2$ overhead, mol. wt. 68–81, containing a small amount of $(CF_3)_2NF$, and 10 g. $(CF_3)_2NF$, b.p. −36 to −25°, mol. wt. 160–170. The column holdup, 4 g., after treatment with alcoholic NaOH to remove any unreacted carbamyl fluoride showed a mol. wt. range of 270–302. Its infrared spectrum agreed with that of known $(CF_3)_2NN(CF_3)_2$, mol. wt. 304. The yield of $(CF_3)_2NF$, based on 20 g. $(CF_3)_2NCOF$, was 60%; that of $(CF_3)_2NN(CF_3)_2$, 13%.

**Reaction of $C_2F_5N{=}C{=}O$ with $AgF_2$.**—Twenty-one grams of $C_2F_5NCO$ (0.13 mole) and 74 g. of $AgF_2$ (0.51 mole) were rocked in an autoclave for 11 hours at 100°. The yellow crude product obtained by vacuum transfer was fractionated, giving 3 g. of $COF_2$ overhead, mol. wt. 66–71, and 13 g. of $C_2F_5NCO$, b.p. −8.5 to −5°, mol. wt. 155–163; the holdup and residue, containing some unreacted $C_2F_5NCO$, were put through aqueous base and dried to give 5.5 g. $(C_2F_5)_2N_2$, mol. wt. 254–271, chromatographic purity 95%, infrared spectrum identical with that of a known sample. The yield of $(C_2F_5)_2N_2$, based on unrecovered isocyanate, was 82%.

**Reaction of $C_2F_5NCO$ with $AgF_2$ in the Presence of HF.**—Thirteen grams of $C_2F_5NCO$ (0.08 mole), 13 g. of $AgF_2$ (0.09 mole) and 2–3 g. of HF (*ca.* 0.1 mole) were rocked in an autoclave for 15 hours at 60°. Vacuum transfer after this time gave only 9 g. of volatile material, mol. wt. 95–167. By pumping, about 10 g. of colorless liquid was obtained which fumed in air, was insoluble in, but very reactive with water and alcohol, and boiled with decomposition at about 90°. Distillation through a small Vigreux column gave a colorless product, b.p. 50–51° (80 mm.). Approximately 3–4 g. of this was transferred *in vacuo* into 2 g. of ethanol and allowed to warm to room temperature. Distillation of the washed and dried product gave a colorless liquid, b.p. *ca.* 55–60° (15 mm.), $n^{25}$D 1.3406. Known values for $C_2F_5NHCOOC_2H_5$[13] are b.p. 66–69° (15 mm.), $n^{25}$D 1.3403. This identification of the ester and the mode of formation of the initial $AgF_2$ reaction product indicate that the latter was the carbamyl fluoride, $C_2F_5NHCOF$.

Twenty grams (0.12 mole) of $C_2F_5NCO$, 5–6 g. of HF (0.25 mole) and 50 g. (0.34 mole) of $AgF_2$ were sealed in an autoclave and rocked at 75° for 48 hours. The contents were then pumped out over several hours and fractionated. There were obtained 1.5 g. overhead (b.p. < −80°), mol. wt. 65 ($COF_2$); 2.5 g., b.p. −9.5 to −7° (mostly $C_2F_5NCO$); 4.5 g., b.p. 0–30°, containing $C_4F_{10}$ and $C_2F_5N{=}NC_2F_5$; and a residue of 6 g. The latter was washed quickly with water and dried, distillation of the dried product giving 3 g., b.p. 135–150°, flat at 146°, $n^{28.5}$D 1.3080. The last product showed a strong –COF band in the infrared at 5.33 $\mu$, and reacted with ethanol to give an ester. The boiling point, spectrum and esterification reaction of the 146° material indicate that it may have been the coupled carbamyl fluoride $(C_2F_5NCOF)_2$. On standing over several months in a corked vial, the material became solid.

**Reaction of $CF_3CONH_2$ with $AgF_2$.**—One hundred twenty grams of $AgF_2$ (0.83 mole) was finely ground and suspended in 200 ml. of fluorocarbon solvent (Minnesota Mining and Mfg. Co. product FC 102) contained in a 500-ml. three-neck flask equipped with stirrer, air condenser, and an arrangement for adding solids out of contact with air. All equipment was thoroughly dried before use. Twenty grams of $CF_3CONH_2$ (0.18 mole) was added in small portions over 1 hour with vigorous stirring. The temperature was allowed to climb to 50–60°, and maintained in that range by intermittent cooling during the addition, then raised to reflux for 0.5 hour. At that time the liquid air tail trap contained 3 g. of bluish solid, mol. wt. 88–89, and the Dry Ice tail trap 31 g. of clear, nile-green liquid, about a third of which turned out to be FC 102 carried through the condenser.

Fractionation of the Dry Ice condensate gave 1.5 g. overhead, partly liquid and partly subliming solid; 3 g., b.p. −57 to −50°, mol. wt. 105–111; 2 g., b.p. −50 to −35°, mol. wt. 110–112; 7 g., b.p. −35 to −30°, mol. wt. 110–111; 4.5 g., b.p. −30 to −20° (temperature readings inaccurate because of slow reflux), mol. wt. 110–112; and 2 g. of holdup and residue, yellow, mol. wt. 111–124.

Infrared spectra were taken on the principal cuts. The over-head and liquid air condensate consisted principally of $SiF_4$ with some $COF_2$; smaller quantities of $CF_3CN$, $CF_3COF$ and $CF_3NCO$ were also present. The −57 to −50° cut was mainly $CF_3COF$, with some $SiF_4$, $COF_2$, $CF_3CN$ and $CF_3NCO$. Both the −35 to 30° and the −30 to −20° cuts were pure $CF_3NCO$, freezing to a crystalline mass and melting very sharply. Their infrared spectra showed only a singlet in the C=N region, and no carbonyl bands. The infrared spectrum of the holdup and residue indicated the presence in small quantity of $CF_3N{=}NCF_3$. Lines primarily used for identification were: $SiF_4$ 9.7, $COF_2$ 5.2, 12.9, $CF_3COF$ 5.3, 7.5, $CF_3CN$ 4.4, $CF_3NCO$ 4.3, 6.9 and $CF_3N{=}NCF_3$ 7.8 $\mu$. The infrared spectrum of $CF_3NCO$ is 4.3(s), 6.9(s), 8.2(sh), 8.3(s), 8.7(s)$\mu$. The yield of $CF_3NCO$ was 58%.

**Reaction of $(CF_3CO)_2NH$ with $AgF_2$.**—The starting material was made either by the method of Smith[14] from $(CF_3CO)_2O$ and $CF_3CONH_2$, or by addition of $CF_3COOH$ to $CF_3CN$, the latter procedure giving a purer product but with erratic variations in yield. The imide when pure was a very hygroscopic solid melting at 84.5–85.5°, rather than a liquid as reported.[14]

Thirty grams (0.21 mole) of $AgF_2$ was suspended in 60 ml. of FC 102 and stirred while 10 g. (0.05 mole) of $(CF_3CO)_2NH$ was added slowly, out of contact with the atmosphere, gaseous products being collected in a liquid air trap. The reaction temperature was maintained at about 60° during the addition, then raised to reflux (*ca.* 100°) for a short time. The condensate in the trap amounted to 5 g. and had a mol. wt. of 103–122. Its infrared spectrum showed all lines for $CF_3COF$ and $CF_3NCO$, plus traces of unidentified products.

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