[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

# The Action of Elementary Fluorine upon Organic Compounds. XX. The Fluorination of Mono-, Di- and Trimethylamine, Ethylenediamine and Ethyleneimine[1]

BY JAY A. GERVASI,[2] MORTON BROWN[3] AND LUCIUS A. BIGELOW

RECEIVED AUGUST 15, 1955

This paper describes the direct fluorination under many conditions of a number of different types of aliphatic amines. Mono-, di- and trimethylamines underwent not only the expected perfluorination, but also simultaneous dealkylation, alkylation and dimerization such that, for example, $(CH_3)_2NH$ gave $CF_3NF_2$, $(CF_3)_2NF$, $(CF_3)_3N$ and $(CF_3)_2N-N(CF_3)_2$, together with other products. It was also shown that $CH_3NH_2$ and $(CH_3)_3N$ did not evolve $N_2$ during fluorination, although in the former case no nitrogen balance could be obtained. Ethylenediamine, in addition to the expected cleavage and dimerization, gave significant amounts of $CF_3N{=}NCF_3$; while 10% of the nitrogen in the sample was evolved as $N_2$. The related $\underbrace{CH_2CH_2NH}$ yielded pure $(CF_3)_2NF$, and much $CF_3N{=}NCF_3$, which has been shown to be stable itself at 500°, stable to fluorine at 400° but to undergo fluorinolysis at 500° to yield $CF_4 + N_2$. Various free radical mechanisms to explain these results have been discussed.

A preceding paper[4] has described the fluorination of acetonitrile, which yielded the interesting compounds $CF_3CF_2NF_2$ and $CF_2{=}NF$, but no elementary nitrogen. This paper extends that work and presents the results of the direct fluorination of a series of representative amines.

Unexpectedly, each of these yielded essentially the same basic products under all conditions studied. They were $CF_4$; an inseparable mixture of $CF_3NF_2 + C_2F_6$; a similar mixture of $CF_3CF_2NF_2 + (CF_3)_2NF$; and a volatile perfluorinated dimer cut, mol. wt. 180–300, together with other products of lesser importance. This indicated that the fluorinations took place by simultaneous substitution, cleavage, dimerization and polymerization, and that the free radical mechanisms involved were similar in all cases.

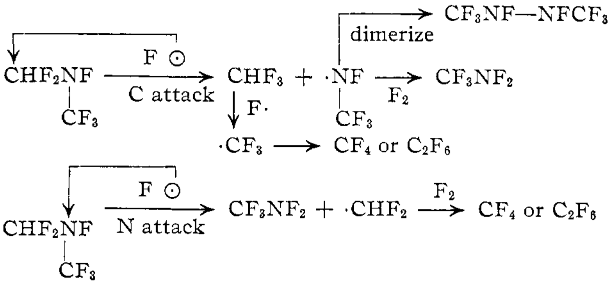
Mono-, di- and trimethylamines were fluorinated in a T-reactor over copper metal, and the most important reactions which took place, other than substitution, were dealkylation, alkylation and dimerization. For example, dimethylamine characteristically yielded under favorable conditions significant amounts of $CF_4$, $CF_3NF_2 + C_2F_6$ (dealkylation), $(CF_3)_2NF + CF_3CF_2NF_2$ (substitution), $(CF_3)_3N$ (alkylation) and volatile dimers, mol. wt. 221–308, half of which consisted of pure $(CF_3)_2N-N(CF_3)_2$, b.p. −2 to −1° (200 mm.),[5] f.p. −61°.

On the other hand, methylamine gave much $CF_4$, $CF_3NF_2 + C_2F_6$ (substitution), $(CF_3)_2NF + CF_3CF_2NF_2$ (alkylation) and nothing else. From Table IA, it is obvious that the greater part of the nitrogen involved was unaccounted for. Consequently a run was made using helium as diluent, and the final exit gases tested for nitrogen by the lithium method,[4] but none was found. The fate of this nitrogen still remains an unsolved problem.

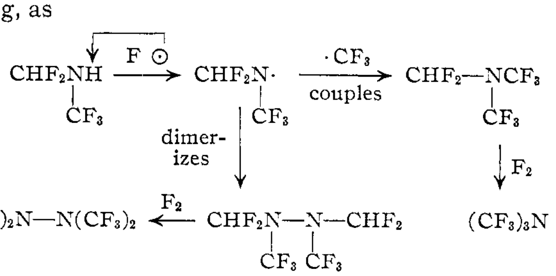
Finally, in this group, trimethylamine produced less $CF_4$, $CF_3NF_2 + C_2F_6$ (small but definite two-stage dealkylation), $(CF_3)_2NF + CF_3CF_2NF_2$ (one-stage dealkylation), $(CF_3)_3N$ (substitution) and volatile dimers, mol. wt. 203–334. There was also definite, although not conclusive, evidence that this dimer fraction contained $CF_3NF-NFCF_3$ or isomers, $CF_3NF-N(CF_3)_2$ and $(CF_3)_2N-N(CF_3)_2$. Also, a qualitative nitrogen balance was obtained, and no elementary nitrogen evolved.

These reactions may be accounted for readily by modern free radical organic chemistry, but such mechanisms usually proceed simultaneously by numerous routes, only a few of which can be detailed here. A fluorine atom may attack hydrogen, carbon or nitrogen in an amine molecule, followed by further fluorination, cleavage, dealkylation, coupling, alkylation or dimerization; while any of these changes may take place at any point during the progressive replacement of hydrogen by fluorine in the molecule.

Selecting arbitrarily the following example, dealkylation may proceed by either carbon or nitrogen attack, as



The carbon attack is highly favored, not only statistically, but also since fluorine and nitrogen do not combine readily. On the other hand, alkylation seems to proceed by an attack upon hydrogen linked either to nitrogen or to carbon, followed by coupling, as



---

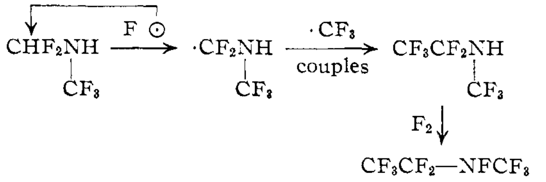
[1] This material was presented at the September, 1954, Meeting of the American Chemical Society in New York, and has been abstracted from portions of the Doctorate Thesis by Jay A. Gervasi and the Master's Thesis by Morton Brown which were presented to Duke University in February and May, 1954, respectively.

[2] Research Assistant, Office of Naval Research, 1950–1951; Allied Chemical and Dye Corporation Fellow, 1951–1953; Research Assistant, Office of Ordnance Research, Fall, 1953.

[3] Research Assistant, Office of Ordnance Research, Spring, 1954. Grateful acknowledgment is also made to the Duke University Research Council for generous support.

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

[5] R. N. Haszeldine, *J. Chem. Soc.*, 102 (1951), has reported the b.p. as 54–56° at 1 atm.



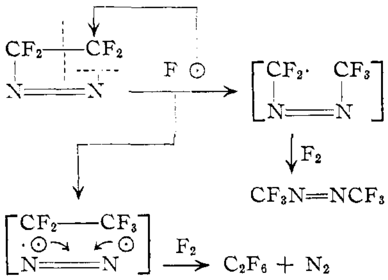
Coupling on nitrogen seems highly favored, and there is little evidence to indicate coupling on carbon. In both dealkylation and alkylation the dimerization of nitrogen radicals appears favored since there is evidence to indicate the formation of $CF_3NF–NFCF_3$ (or isomers) in the former case, and considerable $(CF_3)_2N–N(CF_3)_2$ was actually isolated in the latter.

The fluorination of mono- and trimethylamines may be explained in a similar manner, and all of the products formed in the latter case may be accounted for by the interactions of free radicals expected to be present.

Ethylenediamine was fluorinated in an unpacked concentric ring reactor through the medium of a moderately cool fluorine diffusion flame. Under favorable conditions there were formed $CF_4$; $CF_3NF_2$ without $C_2F_6$ (cleavage); the known isomeric mixture $(CNF_3)_2$; $CF_3CF_2NF_2$, probably without $(CF_3)_2NF$ (alkylation); the known and completely unexpected hexafluoroazomethane $CF_3N{=}NCF_3$ (cyclization and cleavage); and volatile dimers, mol. wt. 175–206. This fluorination was repeated using helium as diluent, and the exit gases tested for nitrogen. It was found that nearly 10% of the nitrogen in the sample had been evolved as such during the fluorination.

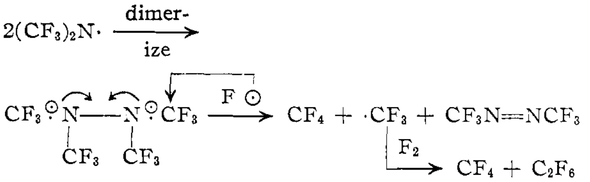
The related ethyleneimine was fluorinated in the new turbulent jet[6] reactor, involving a relatively cool non-diffusion flame. There were formed $CF_4$; $CF_3NF_2$ + $C_2F_6$; nearly pure $(CF_3)_2NF$ (f.p. −171°); again the unexpected $CF_3N{=}NCF_3$ (20%); volatile dimers, mol. wt. 178–218; and higher boiling dimers, mol. wt. 229–327, half of which consisted of pure $(CF_3)_2N–N(CF_3)_2$.

Theoretically the fluorination of the diamine could well lead to the simultaneous formation and cleavage of a cyclic intermediate, as



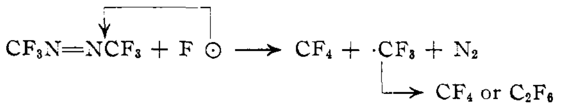
If this cyclization and cleavage are assumed, the production of the unexpected hexafluoroazomethane and also of the elementary nitrogen may be neatly accounted for.

On the other hand, the fluorination of the imine could easily result in dimerization and subsequent fluorinolysis as



It seems probable that the fluorinolysis at cool flame temperatures of a considerable part of the $(CF_3)_2N–N(CF_3)_2$ originally formed should account well for the unexpectedly large proportion of $CF_3N{=}NCF_3$ actually produced.

It has now been possible to accumulate and purify a considerable amount of $CF_3N{=}NCF_3$, and then to fluorinate it over copper metal in a specially designed high temperature reactor. The compound proved very resistant, since it did not undergo cracking even at 500°, nor appreciable fluorinolysis up to 400°. However, at the molar fluorination ratio of 1:1 and 500°, most of the compound did undergo fluorinolysis with the evolution of nitrogen as



From all of our work in this field, it appears that the fluorinolysis of a perfluorinated chain or ring of carbon and nitrogen atoms in which the latter are adjacent will lead to carbon attack, the formation of $CF_3N{=}NCF_3$, and the ultimate evolution of nitrogen. However, if the carbon and nitrogen atoms are alternately placed, as described earlier,[4] it is more likely that the stable $CF_2{=}NF$ will be formed and nitrogen not evolved. Further work in this general field is actively in progress in this Laboratory.

## Experimental

**Apparatus.**—Four different reactors have been used in these studies, namely, the T,[7] the concentric ring,[8] the jet,[6] and the high temperature types. The second of these has been modified as follows. The burner now extended only 4 cm. into the reactor, and was enlarged in diameter to 4.8 cm., while the middle ring was relatively widened to increase the diffusion path, and the central ring was provided with a solid metal core to augment the velocity of the gases at this point. The respective dimensions of the three concentric tubes and the central core were, o.d. 4.8, 4.3, 2.5, 1.8 and i.d. 4.6, 4.0, 2.3 cm. The high temperature reactor consisted of a solid brass rod, 4″ × 10″, with a 0.5″ hole drilled through the center along the main axis. This inner chamber was packed with small sections of copper gauze, and terminated at each end in 3/8″ standard unions, silver-soldered on. A 0.5″ sample inlet union was soldered to the side of the rod 3″ from the fluorine inlet, and a Weston thermometer well 1/8″ × 4″ was drilled in longitudinally. The unit was insulated, wound and lagged so that it could be heated electrically to 600°.

**Materials.**—The mono-, di- and trimethylamines were rated by the manufacturer as 96.5–98.2% pure and were used directly from the cylinders. The ethylenediamine was dried over KOH and rectified in the presence of zinc dust, b.p. 117.5°. The ethyleneimine was prepared from ethanolamine in an over-all yield of 28%, b.p. 55–56°, by the methods of Wenker,[9] and Allen, *et al.*[10]

---

(6) E. A. Tyczkowski and L. A. Bigelow, THIS JOURNAL, **77**, 3007 (1955).

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

(8) E. A. Tyczkowski and L. A. Bigelow, *ibid.*, **75**, 3523 (1953).

(9) J. H. Wenker, *ibid.*, **57**, 2328 (1935).

(10) C. F. H. Allen, F. W. Spangler and E. R. Webster, *Org. Syntheses*, **30**, 38 (1950).

TABLE I

THE RECTIFICATION OF FLUORINATED MONO-, DI- AND TRIMETHYLAMINES

| Fract. | Chief product | Boiling range, °C. | Molecular wt. Obsd. | Molecular wt. Calcd. | Liq. vol. % of total condensate |
|---|---|---|---|---|---|
| A. | $CH_3NH_2$; *R*, 0.054 mole/hr.; *MR*, 5:1:15; *T*, 100°; time 22 hr.; crude 20 cc. | | | | |
| 1 | $CF_4$ | −130 to −129 | 88–91 | 88 | 52 |
| 2 | .... | −98 to −93 | 82–67 | .. | 13 |
| 3 | $CF_3NF_2 + C_2F_6$ | −79 | 118–132 | .. | 13 |
| 4 | $CF_3CF_2NF_2 + (CF_3)_2NF$ | −40 | 172–176 | 171 | 22 |
| B. | $(CH_3)_2NH$; *R*, 0.051 mole/hr.; *MR*, 5:1:15; *T*, 275°; time 10 hr.; crude 23 cc. | | | | |
| 1 | $CF_4$ | −130 to −129 | 87–88 | 88 | 44 |
| 2 | Transition | −129 to −81 | 85–78 | .. | 2 |
| 3 | $CF_3NF_2 + C_2F_6$ | −81 to −79 | 124–129 | .. | 7 |
| 4 | $CF_3CF_2NF_2 + (CF_3)_2NF$ | −39 | 165–168 | 171 | 22 |
| 5 | $(CF_3)_3N$ | −11 | 218–221 | 221 | 11 |
| 6 | Residue | .. | 221–238 | .. | 13 |
| C. | $(CH_3)_3N$; *R*, 0.050 mole/hr.; *MR*, 7:1:21; *T*, 275°; time 12 hr.; crude 41 cc. | | | | |
| 1 | $CF_4$ | −128 | 85–87 | 88 | 22 |
| 2 | .... | −92 to −88 | 86–96 | .. | 5 |
| 3 | $CF_3NF_2 + C_2F_6$ | −79 | 127–134 | .. | 5 |
| 4 | $CF_3CF_2NF_2 + (CF_3)_2NF$ | −40 to −39 | 167–171 | 171 | 12 |
| 5 | Transition | −13 to −11 | 203–224 | .. | 12 |
| 6 | $(CF_3)_3N$ | −11 | 224 | 221 | 20 |
| 7 | .... | 6 to 7 | 210–213 | .. | 10 |
| 8 | .... | 16 to 17 | 241–248 | .. | 5 |
| 9 | Residue | .. | 274–334 | .. | 10 |

**The Fluorination of Mono-, Di- and Trimethylamine.**—In this series a dozen runs were made, using different samples, reactors and operating conditions; but only one characteristic detailed description and data for three representative rectifications will be presented here as follows. Methylamine from the cylinder, controlled by a needle valve and metered by a calibrated flow meter, at the rate (*R*) of 0.054 mole/hr., was diluted with 10 l./hr. of $N_2$, and the mixture led directly into the T-reactor maintained at an equilibrium temperature (*T*) of 100°, where it met and reacted with 0.27 mole/hr. of $F_2$ carried in on 10 l./hr. of $N_2$, such that the molar reaction ratio (*MR*)($F_2$:sample:$N_2$) was 5:1:15, corresponding to a fluorination ratio of 5:1 and a dilution ratio of 1:3. The exit gases were passed over sodium fluoride pellets at about 100° to remove HF, and then condensed, first by Dry Ice and then by liquid air. After 22 hr. roughly 20 cc. of crude product had condensed, which was then passed through a solution containing 5% $NaHSO_3$ and 3% NaOH in a counter-current flow stabilizer, but the loss in all cases was small. Finally the stabilized product was rectified carefully in a Booth–Podbielniak low-temperature fractionating unit with the results shown in the condensed Table I.

Fractions $A_3$, $B_3$ and $C_3$, as well as $A_4$, $B_4$ and $C_4$ represent known inseparable mixtures of the indicated constituents; while fractions $B_6$ and $C_{7-9}$ are the so-called volatile dimers.

**Fraction $C_6$.**—This portion was carefully redistilled and yielded very nearly pure $(CF_3)_3N$, b.p. −10.5°, f.p. −116 to −115°, mol. wt. 224; known b.p. −7 to −6°,[5] mol. wt. calcd. 221.

Fractions $C_{7,8}$ and $_9$ may well have contained $CF_3NF\text{-}NF\text{-}CF_3$ or isomers, mol. wt. (calcd.) 204; $CF_3NF\text{-}N(CF_3)_2$, mol. wt. (calcd.) 254; and the known $(CF_3)_2N\text{-}N(CF_3)_2$, mol. wt. (calcd.) 304.

Run B was repeated for 32 hr. at 285° with similar results and 7 cc. of fraction $B_6$ was thus obtained, which on careful redistillation yielded pure $(CF_3)_2N\text{-}N(CF_3)_2$ (3 cc.), b.p. −2 to −1° at 200 mm., f.p. −61°, mol. wt. 305; known b.p. 54–56°,[5] mol. wt. calcd. 304.

To determine whether or not elementary $N_2$ was being evolved during the fluorination of $CH_3NH_2$, run A was repeated at 275° using helium as diluent, and the stabilized exit gases tested for nitrogen by the lithium method.[4] Since no $NH_3$ was evolved, no $N_2$ was present in the exit gases. Trimethylamine was also fluorinated in the unpacked ring reactor using helium as diluent, but under very different conditions, yet with much the same result, and the exit gases were tested as above, but again no $N_2$ was evolved.

**The Fluorination of Ethylenediamine.**—Twelve different fluorinations of this compound have been run under widely varying conditions, and a detailed description of a representative member of this series follows. Ethylenediamine, diluted with 5.8 l./hr. of $N_2$, was carried from a modified, electrically heated, glass saturator, similar to that previously described,[8] maintained at 70° at the rate of 0.031 mole/hr. into the central ring of the unpacked concentric ring reactor heated to 250°, where it met and reacted with 0.248 mole/hr. of undiluted fluorine coming in through the outer ring. At the same time, however, the middle ring carried 123 l./hr. of barrier $N_2$, such that the molar reaction ratio was 8:1:175, corresponding to a reaction ratio of 8:1 and a dilution ratio of 1:22. Under these circumstances the sample burned with a pale blue diffusion flame, as observed in a test glass reactor and, after 24 hr., roughly 43 cc. of crude product had been condensed by Dry Ice and liquid air in traps provided with 6-mm. stopcocks to reduce back pressure. The volatile portion of this product was stabilized and carefully rectified in the usual manner, with the results shown in Table II.

TABLE II

THE RECTIFICATION OF FLUORINATED ETHYLENEDIAMINE

| Fract. | Chief product | Boiling range, °C. | Molecular wt. Obsd. | Molecular wt. Calcd. | Liq. vol. % of total condensate |
|---|---|---|---|---|---|
| 1 | $CF_4$ | −128 to −109 | 84–89 | 88 | 38 |
| 2 | .... | −96 to −81 | 67–80 | .. | 10 |
| 3 | $CF_3NF_2$ | −78 to −76 | 117–119 | 121 | 10 |
| 4 | $(CNF_3)_2$ | −43 to −40 | 156–160 | 166 | 4 |
| 5 | $CF_3CF_2NF_2$ | −40 to −37 | 166–170 | 171 | 7 |
| 6 | $CF_3N{=}NCF_3$ | −33 to −31 | 165–167 | 166 | 7 |
| 7 | .... | −23 to −2 | 175–206 | .. | 4 |
| 8 | Stbln. loss | ......... | ..... | .. | 7 |
| 9 | Non-volatile | ......... | ..... | .. | 14 |

**Fraction 2.**—This fraction contained a portion, b.p. −91°, mol. wt. 70–85, which appeared frequently during these fluorinations, but has not yet been identified.

**Fraction 3.**—This portion was essentially pure $CF_3NF_2$, known b.p. −76°,[11] mol. wt. calcd. 121. Such material when obtained by the fluorination of the various methylamines (see above) was always contaminated by $C_2F_6$.

**Fraction 4.**—This material was redistilled and yielded the pure known isomeric mixture $(CNF_3)_2$, b.p. −40°,

---

(11) R. N. Haszeldine, *J. Chem. Soc.*, 1966 (1950).

f.p. $-128°$, mol. wt. 166 (calcd. 166) in exact agreement with Ruff.[12]

**Fraction 6.**—Central cut was pure $CF_3N{=}NCF_3$, b.p. $-32°$, f.p. $-133°$, mol. wt. 166; known[13] b.p. $-32°$, f.p. $-132°$, mol. wt. calcd. 166.

**Fraction 7.**—This portion may have contained $(CNF_4)_2$ as $CF_3NF{-}NFCF_3$ or isomer.

The above run was then repeated using helium as diluent and the stabilized exit gases tested for $N_2$ by the lithium method.[4] In this case it was found that 9.8% of the nitrogen entering the reactor had been evolved as $N_2$ during the fluorination. In a blank run 40% of the $N_2$ in a known gas sample could be recovered by this method; and this factor was used in the calculations.

**The Fluorination of Ethyleneimine.**—Purified ethyleneimine was fluorinated in the jet reactor with the top half at 120° and the secondary reactor at 100°. The sample diluted with 5.1 l./hr. of $N_2$ was carried from a glass saturator similar to that previously described[8] maintained at 0° at the rate of 0.028 mole/hr., and then further diluted by 1.8 l./hr. of $N_2$, after which it passed into the reactor through the turbulent jet, where it met and reacted with 0.140 mole/hr. of fluorine such that the molar reaction ratio was 5:1:10. After 12 hr. the crude product, amounting to 28 cc., was collected, stabilized by alkaline bisulfite, and rectified in the usual manner, with the results shown in Table III; while a similar run at the ratio of 4:1:8 gave much the same results.

TABLE III

THE RECTIFICATION OF FLUORINATED ETHYLENEIMINE

| Fract. | Chief product | Boiling range, °C. | Molecular wt. Obsd. | Calcd. | Liq. vol. % of total condensate |
|---|---|---|---|---|---|
| 1 | $CF_4$ | $-129$ to $-116$ | 77–89 | 88 | 7 |
| 2 | .... | $-90$ to $-68$ | 90–132 | .. | 9 |
| 3 | $(CF_3)_2NF$ | $-55$ to $-37$ | 132–179 | 171 | 18 |
| 4 | $CF_3N{=}NCF_3$ | $-36$ to $-27$ | 161–173 | 166 | 20 |
| 5 | .... | $-23$ to $+5$ | 178–218 | .. | 16 |
| 6 | $(CF_3)_2N{-}N(CF_3)_2$ | $-32$ to 0 (200 mm.) | 229–327 | 304 | 14 |
| 7 | Stbln. loss | ........ | ..... | .. | 11 |
| 8 | Residue | ......... | ..... | .. | 5 |

**Fraction 2.**—This portion boiled mostly at $-76°$ and consisted essentially of the inseparable mixture of $CF_3NF_2 + C_2F_6$.

**Fraction 3.**—About two-thirds of this fraction was pure $(CF_3)_2NF$, b.p. $-38°$, f.p. $-171°$, mol. wt. 170–173; known b.p. $-38°$,[14] f.p. $-171°$,[4] mol. wt. calcd. 171.

**Fraction 4.**—At least half of this material had b.p. $-33$ to $-32°$, with an average mol. wt. 165 (see above).

**Fraction 5.**—About one-third of this sample had b.p. $-16$ to $-14.5°$, average mol. wt. 188 (see Paper XXI).

**Fraction 6.**—About half of this portion was pure $(CF_3)_2N{-}N(CF_3)_2$, b.p. $-3$ to $-1°$ at 200 mm., f.p. $-61°$, average mol. wt. 305 (see above).

**The Fluorination of Hexafluoroazomethane.**—Purified $CF_3N{=}NCF_3$, b.p. $-33$ to $-31°$, contained in a small cylinder, was metered at the rate of 0.099 mole/hr., diluted with $N_2$ at the rate of 7.3 l./hr., and the mixture passed into the high temperature reactor described above maintained at 275°, where it met with undiluted fluorine entering at the rate of 0.099 mole/hr., such that the molar reaction ratio was 1:1:3. The product was passed over sodium fluoride at 100°, and after 1 hr. 15 cc. of material had been condensed, which was stabilized by 5% NaOH and rectified in the usual manner; but the unchanged sample was recovered in 92% yield. Similar runs were made at the ratio of 1:1:0 at both 275° and 400°, with the same result, although the contact was short. Finally a run was made at 1:1:0 and 500°, when a reaction took place, and the crude product (9 cc.) was stabilized and rectified in the usual manner with the results shown in Table IV.

TABLE IV

THE RECTIFICATION OF FLUORINATED $CF_3N{=}NCF_3$

| Chief product | Boiling range, °C. | Molecular wt. Obsd. | Calcd. | Liq. vol. % of total condensate |
|---|---|---|---|---|
| $CF_4$ | $-129$ to $-123$ | 86–89 | 88 | 83 |
| $C_2F_6$ | $-82$ to $-75$ | 134–140 | 138 | 6 |
| $CF_3N{=}NCF_3$ | $-34$ to $-28$ | 161–167 | 166 | 11 |

In the above run the final exit gases, swept along by a little diluent helium which had been introduced into the crude product, were stabilized over 10% NaOH + 10% $NaHSO_3$, dried by liquid air, and then passed directly over lithium at 60° for the subsequent determination of their $N_2$ content in the usual manner. In this way 79% of the $N_2$ in the original sample was accounted for as ammonia.

---

[12] O. Ruff and F. Giese, *Ber.*, **69B**, 604 (1936).

[13] O. Ruff and W. Willenberg, *ibid.*, **73B**, 724 (1940).

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

DURHAM, N. C.

---

[CONTRIBUTION FROM THE CARVER FOUNDATION AND THE DEPARTMENT OF CHEMISTRY, TUSKEGEE INSTITUTE]

# Preparation and Properties of Some α-Fluoroethers[1,2]

BY CLARENCE T. MASON AND CHARLES C. ALLAIN

RECEIVED SEPTEMBER 12, 1955

Various metal fluorides were examined as fluorine-for-chlorine exchange agents with $CCl_3CHClOR$. The efficiency of the exchange was found to descend in approximately the order $HgF_2$, TlF, AgF, KF, $Al_2F_6$, $CrF_3$. Compounds of the general formula $CCl_3CHFOR$ and $CH_2FOR$ (where R is Me, Et, Pr, Bu and allyl) were prepared using $HgF_2$ and their physical and chemical properties examined. All attempts to prepare $CH_3CHFOR$ and $CH_2FOCH_2CH{=}CH_2$ were unsuccessful.

While references in the literature are abundant for di- and polyfluoroethers, information on the monofluoroethers is very scarce, and no work at all seems to have been reported on the α-fluoroethers. The purpose of this work was therefore to investigate the preparation and properties of α-fluoroethers.

When heated, the α-halogenated ethers decompose and polymerize into dark viscous mixtures. In exchange reactions between a metal fluoride and halogenated ethers, the difficulty is in finding a metal fluoride which will exchange its fluorine for halogen at a temperature low enough so as to minimize the decomposition of both the reactant and product. Mercuric fluoride was found to exchange its fluorine for the α-chlorine in some halogenated ethers. The reaction was smooth, and little decomposition took place. Compounds of the type $CCl_3CHFOR$ and $CH_2FOR$ (Tables I and II) were prepared.

---

[1] From part of a thesis submitted by Charles C. Allain in partial fulfillment of the requirements for the degree of Master of Science, Tuskegee Institute, 1955.

[2] Presented at the Fall Meeting of the American Chemical Society, September, 1955.