[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Organic Compounds. XVII. The Direct Fluorination of Acetonitrile[1]

BY JOHN A. CUCULO[2] AND LUCIUS A. BIGELOW

Acetonitrile has been fluorinated in the vapor phase over a copper metal packing under a variety of operating conditions At lower fluorination ratios there were formed, quite unexpectedly, only CF_4, C_2F_6, CF_3CHF_2, CF_3CH_2F, CHF_2–CHF_2, CH_3CF_3 and polymeric material containing nitrogen. It was proved conclusively by carrying out a fluorination under these conditions, but using helium as a diluent, that no nitrogen gas was given off as such during the reaction. At higher ratios there were formed CF_4 and C_2F_6, accompanied by highly volatile corrosive $CF_2{=}NF$, together with $CF_3CF_2NF_2$ and highly fluorinated, stable, polymeric products. The perfluoroamine, obtainable in 20% yield at 275°, was stable to an excess of fluorine at 400°; while some of the polymeric material was still stable at 475°, but not at 600°.

This paper is the first of a group to deal with the direct fluorination of typical organic compounds containing additional elements such as nitrogen and sulfur. Acetonitrile was selected to begin this study on account of its availability, stability and relatively neutral character. The fluorination procedure, which has been described in detail previously,[3,4] consisted essentially in permitting known amounts of the sample and fluorine, each diluted with nitrogen, to mingle and react over a copper metal packing, after which the products were freed from hydrogen fluoride, condensed and finally rectified, using precision equipment. The results divided rather naturally into three groups; those obtained under relatively mild operating conditions, as represented by molar fluorination ratios (F_2: sample) of 3:1 or less, those obtained under more vigorous conditions, as at the molar fluorination ratio of 7:1, and the results of high temperature or even destructive fluorinations. Operating temperatures used in the first two groups varied from 60° to 140° without much effect, but in the third group they rose as high as 600° with pronounced if often unexpected results. In the first group it would seem easy to predict the products which should be formed, namely, CH_2FCN, CHF_2-CN, CF_3CN, FCN, $CF_3CF{=}NF$, $CF_3CF_2NF_2$ and perhaps NF_3; but oddly enough not one of these substances was actually produced under these conditions. Instead there was obtained CF_4, C_2F_6, CF_3CHF_2, a mixture of CF_3CHF_2 + CH_3CF_3 (b.p. near −45°), another mixture of CHF_2CHF_2 + CF_3CH_2F (b.p. near −29°), and an intractable polymeric residue containing nitrogen, all in various proportions depending upon the conditions. The first mixture was identified by vapor phase chlorination to form CF_3CF_2Cl and CCl_3CF_3, as well as by fluorination under more vigorous conditions to give only C_2F_6 and CF_3-CHF_2; while the second mixture was determined by chlorination to give CF_2Cl–CHF_2 and apparently a mixture of CF_2Cl–CF_2Cl + CF_3–$CFCl_2$, as well as by fluorination to form only C_2F_6 and CF_3CHF_2, and under still more vigorous conditions only C_2F_6. Since none of the low boiling products contained nitrogen, it was thought that this gas might be escaping as such during the fluorinations. To settle this question a run was made at the molar reaction ratio (F_2:sample:He) of 3:1:9 using helium as the diluent, which had a slightly moderating effect upon the reaction. The exit gases were passed over charcoal at −183° to adsorb any nitrogen present, the desorbed gases subsequently passed over heated metallic lithium to form lithium nitride, and the metal subsequently dissolved in hot water, but no ammonia was evolved. However, when a known mixture of helium and nitrogen, intentionally contaminated by CF_4, was subjected to exactly the same treatment, 60% of the nitrogen present was recovered as ammonia. These results would seem to be conclusive beyond any reasonable doubt.

In the second group the picture outlined above had been materially changed. In every case the exit gases from the terminal liquid air traps now contained a characteristic corrosive substance which was not fluorine, but liberated iodine from potassium iodide, and attacked mercury strongly. At the molar reaction ratio of 7:1:21, all of the fluorohydrocarbons previously isolated seemed to have been converted into CF_4 and C_2F_6, while two new fractions appeared, one boiling near −40°, and the other over a long range up to room temperature with a high molecular weight. The first of these on rectification yielded pure perfluoroethylamine, $CF_3CF_2NF_2$, b.p. −38°, f.p. −183°, which is an inert, colorless gas, not previously described.[4a,1] The isomeric substance $(CF_3)_2NF$, boiling at −37°, which was reported earlier by Thompson and Emeleus,[5] has been found to melt sharply at −171°.[6] The elusive and highly volatile corrosive compound appeared to concentrate in the CF_4 fraction, and especially in portions boiling a little higher than this compound, which also contained subliming SiF_4 from the action of HF on glass. Accordingly material boiling in this range was accumulated, freed from SiF_4 by dilute alkali which did not absorb the corrosive component, and finally rectified in a special still designed to avoid attack on the mercury manometers. This furnished the new[4a,1] pure perfluoroformimide,

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(2) du Pont Experimental Station, Wilmington, Del. Allied Chemical and Dye Corporation Fellow, 1949–1950. Grateful acknowledgment is also made to the Duke University Research Council for financial support.

(3) A. R. Gilbert and L. A. Bigelow, THIS JOURNAL, **72**, 2411 (1950).

(4) F. F. Holub and L. A. Bigelow, *ibid.*, **72**, 4879 (1950).

(4a) Since this paper was submitted for publication, a communication has appeared (R. N. Haszeldine, *Research* **4**, 339 (1951)), announcing among other things the independent preparation of $CF_3CF_2NF_2$ and $CF_2{=}NF$, but no specific experimental procedures or quantitative data other than boiling points were presented.

(5) J. Thompson and J. H. Emeleus, *J. Chem. Soc.*, 3080 (1949).

(6) Both freezing points were measured in this Laboratory by Mr. Jay A. Gervasi.

$CF_2{=}NF$, b.p. −101°, which was a colorless gas with a nauseating odor, condensing to a white solid in liquid air, which liberated iodine from potassium iodide, attacked mercury strongly and was completely absorbed by alkaline bisulfite solution.

In the last group, the acetonitrile was first fluorinated at the reaction ratio of 7:1:21 in the regular reactor, but at a temperature of 275°, which raised the yield of the perfluoroamine ($CF_3CF_2NF_2$) to 20 liq. vol. per cent. of the total condensate, which could almost certainly be increased under optimum conditions. This important observation shows that this interesting compound may readily be prepared in quantity. Then perfluoroethylamine itself was fluorinated over copper metal in a specially designed high temperature reactor at a molar reaction ratio of 1.5:1:1.5, and 400°, but the recovered material was practically all $CF_3CF_2NF_2$, b.p. −39°. Next, samples of polymeric product previously isolated were fluorinated in the same reactor at 3:1:3 and 250°; 6:1:18 and 300°; and 8:1:5 and 300°, but the products in each case were still polymeric. Finally all polymeric material was refluorinated at 6:1:6 and 400°, recycled at 475°, and again at 600°, after which none remained. The combined low boiling cracked products on rectification yielded CF_4 and C_2F_6, but neither $CF_2{=}NF$ nor CF_3NF_2 which had been expected.

The results obtained in the first two groups may readily be accounted for on the assumption that not only most of the incoming acetonitrile, but also all of its simple fluorinated derivatives originally produced, were rapidly polymerized within the reactor by an atomic mechanism according to the general scheme

$$RC{\equiv}N \xrightarrow[\text{HF vapor}]{F\cdot} RCF = N\cdot \xrightarrow{n\text{RCN}} \left[\begin{array}{cc} R & R \\ | & | \\ -C{=}N-C{=}N- \end{array}\right]_n \text{linear or cyclic}$$

where R = $-CH_3$, $-CH_2F$, $-CHF_2$, or $-CF_3$; and also where other chain initiators such as RC=NH or RCH=N· would lead essentially to the same result. The linear conjugated structure is preferred for much of the polymer on account of stability due to resonance, but the highly complex mixture would undoubtedly contain numerous units with adjacent carbon and nitrogen atoms, as well as cyclic structures with aromatic resonance, such as substituted triazines. Inasmuch as the >C=N- group as in $CF_2{=}NF$ does not add fluorine any more readily than a carbonyl group or CO_2, the further action of fluorine atoms on such a conjugated chain would be to split off R· groups, including $\cdot CH_3$, which on dimerization could form all the fluorohydrocarbons and the C_2F_6 isolated under the mild operating conditions. At higher fluorination ratios and temperatures the dealkylated, conjugated chain, perhaps having the form $[-CF{=}N-\,-CF{=}N-]_n$, would be expected to crack apart under the influence of fluorine atoms to yield $CF_2{=}NF$, which, since it would not add fluorine, would accumulate in the product and so be isolated.

It does not appear likely that the $CF_3CF_2NF_2$ could have been produced by the direct addition of fluorine to CF_3CN, since the obvious intermediate product $CF_3CF{=}NF$, which should be corrosive and easily detected, was never found. Nor does it seem probable either that the C–C bond in the nitrile itself was ever cleaved, on account of the total absence of CHF_3 or FCN in the product. Instead, under the stronger operating conditions, portions of the conjugated chain where R = CF_3, probably added fluorine to produce units of the general form,

$$\left[\begin{array}{cccc} CF_3 & & CF_3 & \\ | & & | & \\ -CF- & NF- & CF- & NF- \end{array}\right]_n$$

which on account of the absence of conjugate resonance would then be expected to cleave on further fluorination to yield $CF_3CF_2NF_2$ in preference to splitting off $\cdot CF_3$ radicals, at least to a considerable extent.

Finally, the extraordinarily stable polymeric material which could not be destructively fluorinated under 600°, could well be explained on the basis of portions of the polymeric chain containing adjacent pairs of carbon and nitrogen atoms, either with or without conjugate resonance, or else of cyclic aromatic structures. The above general hypothesis, while admittedly speculative, accounts well for all the observed facts.

Experimental

Apparatus: Standard Set-Up.—The electrically heated, calibrated metal saturator used in this work was equipped with a level regulator and spray trap; while the heated cylindrical reactor was provided with sidearms and completely packed with copper shot. These units were constructed in this laboratory and have been described in further detail by Gilbert[3] and Holub.[4] In operation the sample was carried on a metered current of nitrogen from the saturator into the reactor where it encountered a current of diluted fluorine and reacted over the surface of the metal packing. The exit gases passed over sodium fluoride pellets in a heated tube to remove hydrogen fluoride after which they were condensed in a series of traps sometimes at first by Dry Ice and ultimately by liquid air. The products were subsequently rectified in precision low and high temperature fractionating units.

High Temperature Reactor.—This unit for use above 300° consisted of an electrically heated 2″ × 18″ brass pipe, closed at both ends by sections of 1/4″ brass sheet silver-soldered on, and completely packed with copper shot, all exits being protected from obstruction by pieces of copper screen. About 2″ from the top, two 3/8″ flare fittings were attached opposite to each other for the entrance of sample and fluorine, respectively; while the upper cover carried a 9-in. thermometer well, and the lower one a third 3/8″ flare fitting for the escape of the exit gases. Temperatures above 300° were measured by a calibrated thermocouple. No saturator was used with this reactor, but gaseous samples were displaced through it from a 3.1-l. bulb by means of mineral oil, itself displaced from an adjacent bulb by a metered current of nitrogen. On the other hand when the material was a high boiling polymeric liquid, the reactor was placed horizontally and the sample dropped directly into it from a small glass buret attached through a metal-to-glass seal. A pressure equalizer was connected from the top of the buret to a point just below the stopcock, and this tube also served to bring in a metered current of diluent nitrogen. The exit gases were not passed over sodium fluoride pellets, but were either conducted through a metal line leading directly into the first condensing trap, or else bubbled through a stabilizing alkaline–bisulfite solution contained in a horizontal 45 × 550-mm. glass tube provided with transverse indentations for better mixing. In this case the stabilized gases passed

out through a glass spray trap into the regular condensing ampoules.

Specimen Procedure.—The acetonitrile diluted with 1.35 liters per hour of nitrogen was carried from the saturator, heated to 65°, at the rate of 0.025 mole (1.03 g.) per hour into the reactor, maintained at a base temperature of 70°, where it met and reacted with 0.075 mole of fluorine, carried in on 4.15 liters per hour of nitrogen. The molar reaction ratio (F_2:sample:N_2) was thus 3:1:9, corresponding to a fluorination ratio of 3:1 and a dilution ratio of 1:3. The rise in base temperature was 10°, the operating temperature 80°, and the exit gases were passed through the sodium fluoride tube maintained at about 100°, and finally condensed. After 26 hours of operation, 37 cc. of crude product had been collected, which was again passed over sodium fluoride pellets at reduced pressure, from which treatment 31 cc. of low boiling material and 6 cc. of high boiling residue were recovered. The former was carefully rectified in a Booth–Podbielniak fractionating unit, while the latter could not be distilled without extensive decomposition. The results from this, together with a series of similar runs under various operating conditions, are collected in the following tabulation and arranged in the order of the increasing vigor of the respective fluorinations. All boiling points have been given to the nearest degree and percentages to the nearest 5%.

TABLE I

THE RECTIFICATION OF FLUORINATED ACETONITRILE

Fract.	B.p., °C.	Mol. wt.	Liq. vol. % of low condensate
At 3:1:18; temp. 60°; low, 39 cc.; high, 24 cc.; in 47 hr.			
Ia	−91 to −51	92–112	5
b	−49	99	30
c	−29	103	30
d	>28		35
At 3:1:9 in He; temp. 78°; low, 12 cc.; high, 5 cc.; in 17 hr.			
IIa	−114 to −78	80–85	5
b	−70 to −48	68–101	15
c	−48 to −47	101	15
d	−29 to −27	101	30
e	>28		30
At 3:1:9; temp. 80°; low, 31 cc.; high, 6 cc.; in 26 hr.			
IIIa	−121 to −83	87–90	20
b	−83 to −79	133	10
c	−49 to −46	120–104	30
d	−28 to −24	108–104	10
e	−21 to >0	115–160	10
f	>28		15
At 4:1:12; temp. 82°; low, 53 cc.; high, 10 cc.; in 44 hr.			
IVa	−128	86–88	10
b	−128 to −78	88–107	5
c	−78	134	40
d	−49	122	15
e	−45 to +12	124–192	15
f	>28		15
At 7:1:21; temp. 85°; low, 226 cc.; high, 15 cc.; in 97 hr.; large scale run. Stabilized by passing through 2% NaOH soln.			
Va	−128 to −90	80–126	15
b	−88 to −80	86–136	15
c	−80 to −78	130–140	50
d	−51 to −38	126–167	5
e	−38 to −36	173–175	5
f	−36 to +23	175–259	5
g	>28		5
At 7:1:21; temp. 275°; low, 40 cc.; high, 5 cc.; in 18 hr. Stabilized by passing through 900 cc. 8% NaOH + 600 cc. 6% $NaHSO_3$ soln.			
VIa	−128 to −125	81–88	30
b	−79	133–138	40
c	−40 to −38	170	20

In all runs at fluorination ratios of 4:1 or greater, the low boiling condensate contained a corrosive substance which was not fluorine, but which attacked mercury strongly and liberated iodine from potassium iodide. This gas escaped continuously from the last liquid air trap along with the diluent nitrogen during such runs. At ratios of 3:1 this material was wholly absent.

In a number of the fluorinations listed above the volatile product was passed over hot copper at 250° and then through strong alkali solution in order to remove the corrosive compound completely, if present; but it was demonstrated beyond question that the product was not otherwise materially altered in composition by this treatment in any case. The rectification of unstabilized samples containing the corrosive gas required a special system consisting of a separate manifold carrying ampoules without individual manometers, and an all glass gas density balance. Two specially designed manometers were also provided, one to measure pressures in the column, and the other those in the balance. These manometers were made of capillary tubing except that one arm carried a short wide section within which the mercury meniscus exposed to the sample stood. In operation this meniscus moved but slightly; and since the attack of the corrosive gas formed a protective coating at the undisturbed mercury surface, such a manometer could be used satisfactorily under such circumstances for a considerable time.

General Comment.—A comparison of Runs II and III shows that helium as a diluent moderated the reaction somewhat over nitrogen; which is understandable in terms of the greater mobility of the former gas. A consideration of the results in Runs IV and V indicates that a rise in fluorination ratio from 4:1 to 7:1 at the same dilution ratio of 1:3 had a very marked effect upon the course of the reaction; whereas other experiments, not described, demonstrated that a rise in temperature only, from 82° to 140°, originally thought drastic, had very little effect upon the composition of the product. However a similar comparison of Runs V and VI makes it clear that a really drastic temperature change of nearly 200° at the same fluorination and dilution ratios did have a pronounced effect upon the results.

Fraction IIIc.—An accumulated sample of material similar to this, b.p. −47 to −45°, was carefully redistilled, b.p. −45°, f.p. −107°, mol. wt. 102. A portion was then chlorinated in a 5-liter evacuated bulb illuminated by a 200-watt lamp at the approximate molar chlorination ratio of 1:2.4, as follows. First chlorine was admitted to the bulb until the pressure reached 535 mm., and was followed by 6 liq. cc. of sample, after which the mixture was illuminated for 20 hr. Then the products were withdrawn into a refrigerated ampoule, and subsequently passed through alkaline bisulfite solution, dried and recondensed; from which treatment there was recovered a low boiling portion and a residue not volatile at room temperature, both of which were carefully rectified. The former yielded 4 cc. of pure CF_3CF_2Cl, b.p. −38°, mol. wt. 152 (known b.p. −38°,[7] mol. wt., 154.5); while the latter was almost entirely pure CCl_3CF_3, b.p. 45° to 46°, f.p. 14°, $n^{20}D$ 1.3602 (known b.p. 45.9°, f.p. 14.2°, $n^{20}D$ 1.3610[8]). Then another portion of this sample (about 13 liq. cc.) was fluorinated at the molar reaction ratio of 1.5:1:4.5, operating temp. 120° (rise 15°), in the usual way except that the undiluted sample was displaced through the reactor at a measured rate from the unit described above in connection with the high temperature fluorinator. The product was passed over sodium fluoride, condensed (9 cc.), and rectified, yielding 3 cc. of C_2F_6, b.p. −75°, mol. wt. 136, and 5 cc. of pure CF_3CHF_2, b.p. −48°, mol. wt. 120 (known b.p. −48.5°,[9] mol. wt. 120), and nothing else. Repeated chlorinations and fluorinations of this product under varying conditions always produced essentially the same results. Consequently, the material b.p. −45°, mol. wt. 102, must have been almost entirely a mixture of

(7) E. G. Locke, W. R. Brode and A. L. Henne, THIS JOURNAL, **56**, 1726 (1934).

(8) A. L. Henne and E. G. Wiest, *ibid.*, **62**, 2051 (1940).

(9) D. S. Young, N. Fukuhara and L. A. Bigelow, *ibid.*, **62**, 1171 (1940).

CF_3CHF_2, b.p. −48°, and CH_3CF_3 b.p. −46.7°[10] in the rough proportion of 2:1.

Fraction Ic.—This fraction was combined with a nearly equal amount of similar material and again carefully rectified, b.p. −29°, f.p. −104°, mol. wt. 102. A portion (8 cc.) was then chlorinated as described above at the approximate molar chlorination ratio of 1:1.55, and illuminated for 21 hr. The stabilized, dried product (7 cc.) was rectified and yielded 2 cc. of unreacted sample, b.p. −28°, mol. wt. 104; 2 cc. of CHF_2–CF_2Cl, b.p. −13°, mol. wt. 137 (known b.p. −12°,[11] mol. wt. 137.5); and 3 cc. of presumably CF_2Cl–CF_2Cl + CF_3–$CFCl_2$, b.p. 4°, mol. wt. 168 (known CF_2Cl–CF_2Cl, b.p. 3.8°[7], CF_3–$CFCl_2$, b.p. 3.6°,[12] mol. wts., 171). Then another portion of this sample (about 13 liq. cc.) was fluorinated at the molar reaction ratio of 1.5:1:4.5, operating temp. 112° (rise 10°), in the usual way except that the undiluted sample was displaced through the reactor as described above. The product (originally 9 cc.) was ultimately passed through 400 cc. of 5% alkali soln. to remove a significant amount of subliming SiF_4, which hampered the distillation, and finally rectified. There were formed 2 cc. of C_2F_6, b.p. −78°, mol. wt. 137; 3 cc. of CF_3–CHF_2, b.p. −48°, mol. wt., 122; 1.5 cc. of unreacted material, b.p. −27°, mol. wt. 103, and essentially nothing else. More vigorous fluorination of this sample yielded only C_2F_6. Accordingly the material b.p. −29°, mol. wt. 102, was almost certainly an azeotropic mixture of CHF_2–CHF_2, b.p. −23°,[9] and CF_3–CH_2F, b.p. −26.1°.[13]

Fraction Ve.—A sample of similar material from a preceding run was slowly and carefully redistilled, yielding pure $CF_3CF_2NF_2$, b.p. −38°, f.p. −183°. It was an inert, colorless gas, condensing to a colorless liquid, which solidified very slowly in liquid air and did not attack mercury.

Anal.[14] Calcd. for C_2NF_7: F, 77.8; mol. wt., 171. Found: F, 77.9, 78.2; mol. wt., 171.

Fractions Va and b.—The portions of these fractions remaining after certain other experiments were combined, slowly bubbled through 3% NaOH soln., dried and rectified, using the special system described above (following. Table I). First impure CF_4 came over, then a middle portion (3 cc.), b.p. −108° to −91°, mol. wt. 85–81, followed by impure C_2F_6. The central cut was redistilled very slowly, and yielded a main portion which was pure $CF_2{=}NF$, b.p. −101°. This gas which condensed to a colorless liquid and finally froze to a white solid in liquid air, attacked mercury strongly, liberated iodine from KI solution, was completely absorbed by alkaline bisulfite soln., had a pungent nauseating odor, and was presumably very toxic.

Anal.[14] Calcd. for CNF_3: F, 68.66; mol. wt., 83. Found: F, 68.51; mol. wt., 83.

Fractions VIb and c.—The first of these, essentially C_2F_6, was shown to contain no hidden CF_3NH_2 by complete conversion to the known[15] azeotrope of C_2F_6 + C_2H_6, b.p. −94°, mol. wt., 62. The second, essentially $CF_3CF_2NF_2$, was obtained in 20% yield, which could almost certainly be increased under optimum operating conditions.

Run II.—This run was conducted in helium as a diluent, in order to prove conclusively whether or not nitrogen gas was evolved as such during the fluorination.

First a blank run was made and, in order to simulate actual conditions as closely as possible, an artificial gas mixture in the approximate volume ratio of $He:N_2:CF_4$ as 18:1:1 was passed first through two liquid air traps, and then through two more traps filled with gas mask charcoal, also cooled by liquid air, all for a period of 7 hr. Then the adsorbed gases, containing considerable CF_4, were desorbed by heating the charcoal to 350° for 6 hr. using electric jacket heaters. Next the desorbed gases were repeatedly displaced over metallic lithium contained in an electrically heated V tube at 60–70° until no further contraction took place. Finally the mixture of lithium and lithium nitride was dropped little by little into hot water in a modified Kjeldahl apparatus, and the ammonia evolved determined volumetrically in the usual way. Within reasonable limits of error, the nitrogen in the desorbed gases was quantitatively recovered as ammonia in this way, and represented about 60% of the nitrogen in the original sample, the remainder, together with most if not all of the helium, having been displaced from the charcoal surface by the CF_4 intentionally present in the sample. In the actual fluorination the exit gases from the condensing traps were adsorbed, desorbed and passed over lithium exactly as before. However, when the metal was dissolved in water, essentially no ammonia was evolved; furthermore in a somewhat similar manner no nitrogen whatever could be found dissolved in the condensed fluorinated products. These results prove beyond doubt that no elementary nitrogen was evolved during the fluorination of acetonitrile under these conditions.

Destructive Fluorinations.—First an 8-cc. sample of perfluoroethylamine was displaced through the high temperature reactor (see apparatus) during 1 hr., and fluorinated at the approximate molar reaction ratio of 1.5:1:1.5, and 400°. The exit gases were stabilized by alkaline bisulfite solution, dried (6 cc.), and rectified; but almost the entire product was unchanged sample, b.p. −39°, mol. wt. 170. In a similar run using the standard reactor at 300°, about one-third of the sample was decomposed into C_2F_6 and unknown products.

Next Fraction Vf (15 liq. cc.) was fluorinated in the high temperature reactor during 1 hr. at 3:1:3 and 250°, but the only significant product (4 cc.) b.p. −6° to +10°, mol. wt. 227, was still polymeric. Then Fraction Vg was dropped into the horizontally placed reactor (see apparatus) and fluorinated at 6:1:18 and 300°; but the product was still polymeric and was recycled at 8:1:5 and 300°. This time the stabilized rectified product nearly all came over at 61° to 62°, mol. wt. 366.

Finally all high boiling residues were combined and fluorinated as before at 6:1:6 and 400°. The surviving high boiling products were recycled at 475° and then 600°, after which none remained. The low boiling products stabilized only by 2% NaOH soln., were combined and rectified, yielding CF_4 and C_2F_6 but no $CF_2{=}NF$ nor CF_3NF_2, as had been expected.

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(10) A. L. Henne and M. W. Renoll, THIS JOURNAL, **58**, 889 (1936).

(11) A. L. Henne and E. C. Ladd, *ibid.*, **58**, 402 (1936).

(12) A. L. Henne and R. P. Ruh, *ibid.*, **70**, 1025 (1948).

(13) Private communication from Dr. S. R. Dietrich, The du Pont Company, Wilmington, Delaware.

(14) Analysis by the Huffman Micro-analytical Laboratories, Denver, Colorado.

(15) J. D. Calfee, N. Fukuhara and L. A. Bigelow, THIS JOURNAL, **61**, 3552 (1939).