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Fluorocarbon Nitrogen Compounds. IV.¹ The Reaction of Metallic Fluorides with Carbon-Nitrogen Unsaturation in Perfluoro-2-azapropene²

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Several metallic fluorides react with the carbon-nitrogen unsaturation in perfluoro-2-azapropene, $\text{CF}_3\text{N}=\text{CF}_2$, although the reaction is not usually simple addition of fluorine. Activity decreases in the order: AgF_2 , AgF , HgF_2 , CoF_3 , PbF_4 , MnF_3 . No reaction is shown by NaF , TiF_4 or SbF_3 , while SbF_5 causes fragmentation. The activities of HgF_2 and MnF_3 in this series do not correspond to those previously found in the fluorination of hydrocarbons. Silver difluoride at room temperature gives both the azomethine dimer, $(\text{CF}_3)_2\text{NCF}=\text{NCF}_3$, and the substituted hydrazine, $(\text{CF}_3)_2\text{NN}(\text{CF}_3)_2$. At higher reaction temperatures both $\text{CF}_3\text{N}=\text{CF}_2$ and $(\text{CF}_3)_2\text{NCF}=\text{NCF}_3$ are converted to $(\text{CF}_3)_2\text{NF}$, but $(\text{CF}_3)_2\text{NN}(\text{CF}_3)_2$ does not react further. Under the conditions used, lead tetrafluoride gives both the dimer and the hydrazine, but not $(\text{CF}_3)_2\text{NF}$; CoF_3 gives the hydrazine and $(\text{CF}_3)_2\text{NF}$, but no dimer; and AgF gives only the dimer. Mercuric fluoride is atypical and adds as such to the carbon-nitrogen double bond to yield $(\text{CF}_3)_2\text{N}-\text{Hg}-\text{N}(\text{CF}_3)_2$. Inert, hydrated fluorides produce $\text{CF}_3\text{N}=\text{C}=\text{O}$. Antimony pentafluoride gives only fragments such as CF_4 .

The work of Nerdel and of Hückel³ seemed to indicate that HgF_2 might be quite effective in adding fluorine across the carbon-nitrogen double bond of perfluoro-2-azapropene, $\text{CF}_3\text{N}=\text{CF}_2$ (I). When this reaction was attempted, the sole product was found to be the mercury derivative of bis-(perfluoromethyl)-amine, $(\text{CF}_3)_2\text{N}-\text{Hg}-\text{N}(\text{CF}_3)_2$ ⁴; however, this result was sufficiently interesting so that a study of other metallic fluorides with I was initiated. This paper reports the results of that study.

No other fluoride has been found to add *in toto* across the double bond, but most of those fluorides which have been used previously in fluorination of hydrocarbons were also reactive toward I. Silver difluoride reacted at room temperature to give mainly the azomethine dimer, mol. wt. 266, b.p. 39°, and a smaller amount of an inert compound, mol. wt. 304, b.p. 31°. Hauptschein⁵ has considered the most probable structures of this dimer to be either $(\text{CF}_3)_2\text{NCF}=\text{NCF}_3$ (II), or $\text{CF}_3\text{NCF}_2\text{CF}=\text{NCF}_3$ (III). We believe that II is correct in view of these three independent lines of evidence.

In the first place, an NF bond, present in III but not in II, is difficultly formed except in a highly active fluorinating environment. The dimer produced here was identical with the product formed by ultraviolet irradiation of a mixture of ethylene oxide and I,⁵ by pyrolysis of $(\text{CF}_3)_2\text{NCOF}$ over activated charcoal,⁶ by reaction of $(\text{CF}_3)_2\text{NHgN}(\text{CF}_3)_2$ with sulfur,⁶ and by reaction of I with $\text{O}(\text{CF}_2\text{CF}_2)_2\text{SF}_4$.⁶ It is unlikely that an NF bond would be formed in all these cases, particularly in

the presence of hydrogen-containing compounds such as ethylene oxide.

The second bit of evidence deals with the direction of addition to I. In all known addition reactions of this compound, fluorine becomes attached to carbon and the rest of the addend to nitrogen. These reactions include formation of $(\text{CF}_3)_2\text{NH}$ from I and HF ,⁷ $(\text{CF}_3)_3\text{N}$ from I and CF_3SF_6 ,⁸ and $[(\text{CF}_3)_2\text{N}]_2\text{Hg}$ from I and HgF_2 .⁴ Moreover, in both nucleophilic and free radical reactions of the related perfluoroolefins C_3F_6 and *i*- C_4F_6 , the terminal CF_2 group is the point of attack. Structure II is in accord with these data, while III would require the opposite direction of addition.

Finally, the nuclear magnetic resonance (n.m.r.) spectrum agreed better with structure II than with III. Five peaks should result from III, corresponding to CF_3-NF , $\text{CF}_3-\text{N}=\text{}$, $-\text{CF}_2-$, $=\text{CF}-$ and $-\text{NF}-$. Resonance of the two CF_3 peaks would be very similar, and that of the CF and NF groups so diffuse because of spin-spin interaction that they might not be easily detectable; however, that of the CF_2 group should be strong enough for recognition. Structure II should give only two closely similar peaks for the CF_3 groups and a weaker, diffuse peak for the CF. The actual n.m.r. spectrum showed a close pair of doublets, intensities 2:1, in the CF_3 region, a small, broad structure with a large negative α -value compatible with a $=\text{CF}$ group, and nothing else.

From these considerations, structure II, $(\text{CF}_3)_2\text{NCF}=\text{NCF}_3$, seems greatly more probable than III for the dimer.

Although the molecular weight and elemental analysis of the second product from the AgF_2 reaction corresponded to the saturated dimer, $(\text{CF}_3)_2\text{NCF}_2\text{NCF}_3$, its n.m.r. spectrum showed all the fluorines to be equivalent, with the α -value indicating identical CF_3 groups. The only structure which fulfills these requirements is that of the hydrazine, $(\text{CF}_3)_2\text{NN}(\text{CF}_3)_2$ (IV), and comparison of the infrared spectrum of the product with that of

(1) For the preceding paper in this series, see J. A. Young, S. N. Tsoukalas and R. D. Dresdner, *THIS JOURNAL*, **80**, 3604 (1958).

(2) This material was presented at the 134th Meeting of the American Chemical Society, Chicago, Ill., September 8-12, 1958. The work was supported by the Chemistry Branch of the Office of Naval Research, and reproduction of all or any part of this paper is permitted for purposes of the United States Government.

(3) F. Nerdel, *Naturwiss.*, **39**, 209 (1952); W. Hückel, *Nachr. Akad. Wiss. Göttingen, Math.-physik. Klasse*, No. 1, 55 (1946); *C. A.*, **44**, 4359 (1950).

(4) J. A. Young, S. N. Tsoukalas and R. D. Dresdner, *THIS JOURNAL*, **80**, 3604 (1958).

(5) M. Hauptschein, M. Braid and F. E. Lawlor, *J. Org. Chem.*, **23**, 323 (1958).

(6) Unpublished work done in this Laboratory.

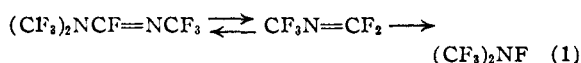
(7) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 2532 (1955).

(8) R. D. Dresdner, *THIS JOURNAL*, **79**, 69 (1957).

(9) This spectrum was furnished by Dr. L. A. Bigelow of Duke University.

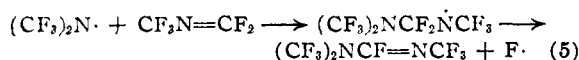
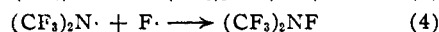
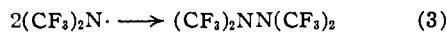
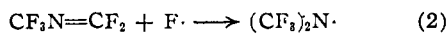
a known sample⁹ showed that the two compounds were indeed identical.

At 100° with AgF₂, Compound I was converted to a mixture of IV and (CF₃)₂NF (V), no dimer remaining after reaction at this temperature. When heated with AgF₂ at 100°, the dimer was converted to a mixture of IV and V, but IV itself did not react further when heated separately with AgF₂ at 100°. Fluorination of the dimer to (CF₃)₂NF probably does not proceed *via* attack on the double bond, since neither the saturated product (CF₃)₂NCF₂NFCF₃ nor the dimer cleavage products (CF₃)₃N and CF₃NF₂ were detected, while complete cleavage of any (CF₃)₂NCF₂NFCF₃ formed as an intermediate seems improbable. Perhaps, under the reaction conditions, an equilibrium exists between I and II, so that the formation of (CF₃)₂NF actually takes place only from I, as shown in reaction 1. Irreversible formation of



V would then account for eventual disappearance of the dimer. The fact that IV was detected in fluorination of the dimer supports this assumption, since the hydrazine could not be formed directly from II but should be formed from the intermediate I.

It is tempting to predicate formation of all three compounds: dimer, hydrazine and (CF₃)₂NF, on the basis of a perfluorodimethylamino radical, as in reactions 2-5.



Although reactions 2, 3 and 4 are quite probable, 5 is less so. If the radical in equation 5 were actually formed, its subsequent reactions should produce either a coupled product [(CF₃)₂NCF₂NCF₃]₂¹⁰ or the compound (CF₃)₂NCF₂NFCF₃. Neither of these was detected. Moreover, the requisite elimination of fluorine from the CF₂ group of this radical to form the dimer, under such mild conditions, has no precedent in fluorocarbon chemistry. Although the CF₂ is situated between two nitrogen atoms and might therefore be expected to be abnormally reactive, it has been found¹¹ previously that the stability of a CF₂ group between two hetero atoms, as in the compound C₂F₅NCF₂OCF₂CF₂, is not materially reduced.

Thus, although proposed formation and reaction of the (CF₃)₂N· radical account quite well for (CF₃)₂NF and (CF₃)₂NN(CF₃)₂, dimerization by the same mechanism is very doubtful, particularly as the latter process can occur, as shown previously, in the absence of any strong fluorinating agent.

Three other fluorides gave essentially the same scheme of reaction, although the product distribution varied. Cobalt trifluoride reacted at 100°

(10) Cf. G. O. Pritchard, *et al.*, *Trans. Faraday Soc.*, **52**, 849 (1956); J. R. Dacey and D. M. Young, *J. Chem. Phys.*, **23**, 1302 (1955), concerning coupling of the (CF₃)₂NNCF₃ radical.

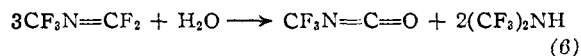
(11) J. A. Young, T. C. Simmons and P. W. Hoffmann, *THIS JOURNAL*, **78**, 5637 (1956).

to give (CF₃)₂NN(CF₃)₂ and (CF₃)₂NF, with traces of cleavage to NF₃ and CF₄, but no (CF₃)₂NCF=NCF₃. Lead tetrafluoride gave IV and II, but no V, even at 250°. In both these cases, unreacted azomethine was recovered after 15 hours at 250°. Silver monofluoride, AgF, proved to be almost as reactive as AgF₂. At room temperature a 56% yield of dimer was obtained after three days, and at 200° conversion to II was complete except for a small amount of CF₃NCO, whose formation must be ascribed to impurities in the AgF. Since there was no contamination by IV, this would seem to be the best method of preparing pure II.

No reaction was observed at 250° with NaF, SbF₃ or TiF₄; MnF₃ gave only a trace of II at 250° and neither IV nor (CF₃)₂NF; however, isolation of an appreciable quantity of (CF₃)₂NH indicated either that conditions were not completely anhydrous during the reaction or that some hydrogen-containing impurities were present.

Antimony pentafluoride at 25° gave no indication of reaction with I. At 100°, reaction occurred to give mainly CF₄, the only product identified. The fate of the nitrogen is unknown.

Haszeldine has found that Compound I can be converted to CF₃NCO by reaction with water,¹² although the conditions he described would be difficult to apply on a preparative scale. A more convenient method of achieving the same result is to heat I with a hydrated fluoride. Thus, an estimated 83% yield of isocyanate was obtained by reaction of I and CuF₂·2H₂O at 100°, the chief disadvantage of this method as a preparation of the isocyanate being the large amount of I which acts as an HF acceptor, as shown in reaction 6.



Experimental

Metallic fluorides were purchased from both Harshaw Chemical Co. and General Chemical Co. Loading of the fluoride into the autoclave was carried out in a dry-box, azomethine being added subsequently by means of a vacuum system. The general procedure was to rock the autoclave at the desired temperature for a given time, remove the volatiles *in vacuo*, and determine their molecular weight range. If substantial reaction was indicated, the crude product was then fractionated; if not, it was returned to the autoclave and rocked at a higher temperature.

The azomethine was prepared by pyrolysis of (CF₃)₂NCOF either in an autoclave at 400° or by passage at 600-650° through a nickel tube packed with NaF pellets; the latter method was superior for large quantities. Infrared spectra were taken on a Perkin-Elmer double beam instrument, using a 5-cm. gas cell loaded *in vacuo*. Gas phase chromatograms were taken on a Perkin-Elmer Fractometer; good resolution was obtained using the ethyl ester of Kell-F acid 8114 as a stationary phase, on Celite packing.

Reaction of CF₃N=CF₂ and AgF₂.—Twenty-four grams of I (0.18 mole) and 45 g. of AgF₂ (0.31 mole), on standing overnight at room temperature, gave 24 g. of product, mol. wt. 240-274. An infrared spectrum showed the presence of both (CF₃)₂NN(CF₃)₂ and (CF₃)₂NCF=NCF₃. When reheated at 100°, this 24 g. gave 14 g. (45%) of (CF₃)₂NF, mol. wt. 171, b.p. -36°; and 5 g. of (CF₃)₂NN(CF₃)₂, mol. wt. 306, b.p. 31-33°, *n*_D²⁰ 1.2408. Known values for mol. wt. and b.p. of these two compounds are, respectively, 171, -37°, and 304, 32°. A chromatogram showed the hydrazine to be 98% pure. No fluoride ion test was obtained when it was treated with warm 30% NaOH solution, and no unsaturation was shown in the infrared spectrum. The latter agreed with a spectrum of known IV furnished

(12) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 3428 (1956).

by Dr. L. A. Bigelow, of Duke University except for a weak line at about 5.3μ in his sample which may be ascribed to traces of unsaturated impurities.

Anal. Calcd. for $C_4F_8N_2$: C, 15.8; F, 75.0. Found: C, 16.1; F, 74.8.

The $(CF_3)_2NF$ was identified by n.m.r. and mass spectroscopy in addition to molecular weight and boiling point. All the expected peaks in both spectra were observed. It gave a strong iodine test when bubbled through aqueous KI solution.

The dimer, when present with IV, was identified by correspondence of its infrared spectrum with that of a known pure sample made by pyrolysis of $(CF_3)_2NCOF$ over activated charcoal and having these properties: chromatographic purity >99%, n_D^{25} 1.2596, mol. wt. 265 (theory 266), b.p. 39° .

Reaction with PbF_4 .—After 72 hours at 50° , the highest mol. wt. on the crude product from 60 g. of PbF_4 (0.21 mole) and 19 g. of I (0.14 mole) was 137. After 40 hours at 150° , the same reactants gave 6 g. of unreacted I, mol. wt. 128–134 (theory 133), and 8 g. boiling above 25° , mol. wt. 280–295. After 15 hours at 200 – 250° , 22 g. of I gave 9 g. of unreacted I, mol. wt. 129–133, b.p. -32 to -26° , and 9 g. boiling above 25° . Fractionation of the combined higher boiling cuts gave 11 g., b.p. 32 – 34° , mol. wt. 299–303. Chromatographic and infrared examination showed $(CF_3)_2NCF=NCF_2$ present to the extent of about 10%, the remainder being IV. No $(CF_3)_2NF$ was found.

Reaction with CoF_2 .—Thirty-three grams of I (0.25 mole) and 56 g. of CoF_2 (0.50 mole) showed no pressure drop at 50° . After 15 hours at 100° , about 1.5 g. boiling above 25° was obtained. After 20 hours at 250° , fractionation gave 4 g. of overhead (Dry Ice condenser) which was liquid in liquid air and probably consisted of a mixture of CF_4 and NF_3 ; 16.5 g. of $(CF_3)_2NF$, mol. wt. 169–170, b.p. -37 to -35° ; and 12 g. of IV, mol. wt. 299–304, b.p. 32° . The IV was spectroscopically free of dimer, while chromatographic and infrared examination showed about 16% unreacted I in the $(CF_3)_2NF$.

Reaction with NaF, TiF_4 , MnF_2 and SbF_3 .—After forty hours at 250° , neither IV nor $(CF_3)_2NF$ was detected in the reaction products from TiF_4 , MnF_2 and SbF_3 . A trace of dimer was found with MnF_2 , but the main product was $(CF_3)_2NH$, mol. wt. 152 (theory 153), formed in about 14% yield and identified by means of its infrared spectrum. The rest of the azomethine, in all three cases, was recovered intact. The lack of activity of NaF is inferred from the fact that it can be used as a packing for pyrolysis of $(CF_3)_2NCOF$ at 600 – 650° without forming any products other than COF_2 and I.

Reaction with AgF .—Twenty-five grams of AgF (0.2 mole) and 24 g. (0.18 mole) of I were allowed to stand 3 days at room temperature. Fractionation of the contents then gave 6 g. of unreacted I and 14 g. of II, b.p. 36 – 39° ,

spectrum identical with that of known II. No IV was present.

A duplicate run at 200° for 18 hours was made. Fractionation gave 2 g. of overhead (ice-water condenser) which was found to be pure $CF_3N=C=O$ by infrared examination. No unreacted I was present. Formation of the isocyanate must be ascribed to impurities present, probably in the silver fluoride. All the rest of the crude product had b.p. 37 – 39° , and was found to be pure II.

Reaction with SbF_3 .—Twenty-seven grams of I (0.20 mole) and 38 g. of SbF_3 (0.18 mole) were allowed to stand at room temperature overnight. No change in pressure was observed. After heating 15 hours at 100° , only 13 g. of very volatile material was recovered. This showed a mol. wt. of 88–93, unchanged by treatment with aqueous alkali. By comparison of its infrared spectrum with that of a known sample, it was found to be CF_4 .

Reaction of $(CF_3)_2NCF=NCF_2$ and AgF_2 .—Nineteen grams of pure II (0.07 mole) and 25 g. of AgF_2 (0.17 mole) were rocked at 100° for 24 hours. Fractionation of the volatile product gave 9 g. of $(CF_3)_2NF$, b.p. -37 to -34° , mol. wt. 169, 172, and 6 g. boiling above room temperature, n_D^{25} 1.2502. This figure is intermediate between those for pure II (1.2596) and IV (1.2408). An infrared spectrum showed all the lines for both of these compounds, and a chromatograph showed the presence of two components in approximately equal amounts.

Reaction with $CuF_2 \cdot 2H_2O$.—Thirty grams of I (0.22 mole) and 7.5 g. of $CuF_2 \cdot 2H_2O$ (0.11 mole) were rocked at 50° for three hours, then at 100° for 15 hours. Fractionation gave 4 g., mol. wt. 114–117, b.p. -37 to -34° ; 4 g., mol. wt. 118–131, b.p. -34 to -25° ; and 18.5 g. of $(CF_3)_2NH$, mol. wt. 153, b.p. -6 to -4° . The first two fractions apparently contained both $CF_3N=C=O$ (mol. wt. 111, b.p. -36°)¹¹ and unreacted I (mol. wt. 133, b.p. -33), and gave all infrared spectral lines for both components. On the basis of the observed molecular weights of the fractions, the yield of isocyanate was about 83% of theory. No attempt was made to find optimum conditions for the reaction.

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