

The hydrogen ions, which act as a catalyst, are omitted for the sake of convenience. These are almost similar to that proposed in the case of oxida-

tion of monohydric alcohols.^{20,21,25}

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

Fluorocarbon Nitrogen Compounds. III.¹ Some Reactions of Bis-(trifluoromethyl)-amine, $(\text{CF}_3)_2\text{NH}$ ²

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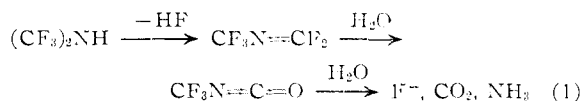
Because of the reduction in base strength caused by the two CF_3 groups, bis-(trifluoromethyl)-amine, $(\text{CF}_3)_2\text{NH}$, does not react normally with the usual amine reagents. In most reactions it tends to reverse the method of synthesis and revert to $\text{CF}_3\text{N}=\text{CF}_2$ and HF; however, it can be nitrated to give $(\text{CF}_3)_2\text{N}\cdot\text{NO}_2$. Reaction of the mercury derivative, $(\text{CF}_3)_2\text{N}\cdot\text{HgN}(\text{CF}_3)_2$, which is made indirectly by addition of HgF_2 to $\text{CF}_3\text{CF}=\text{CF}_2$, with chlorine or bromine gives the corresponding $(\text{CF}_3)_2\text{N}\cdot\text{X}$ derivatives. These cannot be made by direct halogenation. $(\text{CF}_3)_2\text{NBr}$ adds easily across the double bond of $\text{CF}_3\text{CF}=\text{CF}_2$. With inorganic halides of the type MCl_3 , the products are HCl , MF_3 and $\text{CF}_3\text{N}=\text{CCl}_2$.

Although hydrocarbon alkyls of nitrogen form only one series of compounds, the amines (RNH_2 , R_2NH , R_3N), perfluoroalkyls of nitrogen form two series, the nitrides (R_FNF_2 , $(\text{R}_F)_2\text{NF}$, $(\text{R}_F)_3\text{N}$) and the amines (R_FNH_2 , $(\text{R}_F)_2\text{NH}$, $(\text{R}_F)_3\text{N}$). The tertiary compounds in the two fluorocarbon series are obviously identical and are properly classed with the inert nitrides, while the primary amines apparently lose HF so easily that none has yet been isolated as such. Of the true fluorocarbon amines, therefore, only the secondary compounds are available for study. Although fluorocarbon secondary amines have been known since 1940, when Ruff inadvertently prepared $(\text{CF}_3)_2\text{NH}$,⁴ very little has been published concerning their chemistry. This paper describes some reactions and derivatives of the first member of the series, $(\text{CF}_3)_2\text{NH}$.

Bis-(trifluoromethyl)-amine (I), which was prepared easily by addition of HF to perfluoro-2-azapropene, $\text{CF}_3\text{N}=\text{CF}_2$ (II), boils at -6° , twelve degrees lower than dimethylamine. This boiling point lowering is presumably due to decreased hydrogen bonding; the reduced basicity of the nitrogen atom, of which this is one indication, is a chief cause of the wide chemical dissimilarity between the two compounds. Compound I did not form a hydrohalide with HCl and did not give a solid addition product with boron trifluoride, being in the latter respect even less basic than II. It did not react under normally mild conditions with the acid chloride or anhydride of trifluoroacetic acid and could be distilled unchanged from its solution in anhydrous CF_3COOH , although in the last case it became necessary to heat the solution consider-

ably above room temperature in order to drive off the amine completely.

In contrast to its unreactivity toward the usual amine reagents, compound I was entirely destroyed by exposure to water and aqueous acids or bases. The decomposition probably proceeds by initial loss of HF and subsequent hydrolysis of the II so formed, according to equation 1.



There is considerable evidence in support of this sequence,⁵ which includes intermediate isocyanate formation, rather than that originally proposed by Barr and Haszeldine,⁶ in which $\text{CF}_3\text{N}=\text{CF}_2$ was thought to be converted by water directly to CF_3NH_2 and COF_2 . In the present work, if conditions were not completely anhydrous during nitration, formation of II from I could be observed (step 1). Furthermore, II could be converted to the isocyanate by careful treatment with water (step 2), either by reaction in the vapor phase at low pressure⁶ or, better, by heating II with a slowly acting source of water such as a hydrated metallic fluoride.⁷ The first two steps of this hydrolysis mechanism therefore can be considered to be experimentally verified. Its further course is less well established, but may involve either degradation through a carbamic acid structure,⁵ or antecedent hydrolytic attack on fluorine.⁸ All the fluorine is eventually converted to fluoride ion.

Related to this series is perfluorodimethyl carbamyl fluoride, which is thought to decompose by way of the same intermediates, as in reactions 2 and 3.

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

(6) D. A. Barr and R. N. Haszeldine, *ibid.*, 1881, 2532 (1955).

(7) Details of this preparation will be presented in a forthcoming paper.

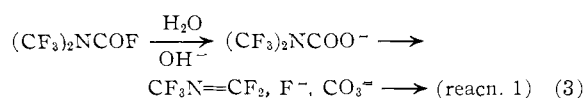
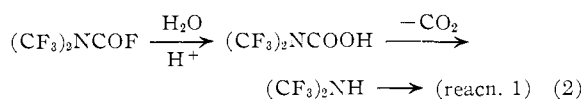
(8) R. L. Danuley and R. G. Taborsky, *J. Org. Chem.*, **22**, 77 (1957).

(1) For the preceding paper in this series, see J. A. Young and R. D. Dresdner, *This Journal*, **80**, 1889 (1958).

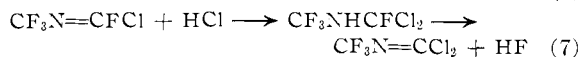
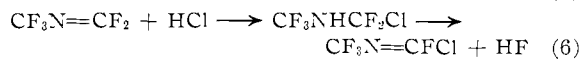
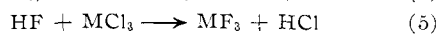
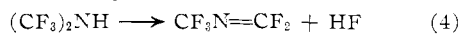
(2) Presented before the Southeast Regional Meeting of the American Chemical Society at Durham, N. C., Nov. 14-16, 1957. This work was supported by a grant from the Office of Naval Research, and reproduction in whole or in part is permitted for any purposes of the United States Government.

(3) This paper includes work done by Skevos N. Tsoukalas in partial fulfillment of the requirements for the M.S. degree, University of Florida.

(4) O. Ruff and W. Willberg, *Ber.*, **73**, 721 (1940).



Facile loss of HF from I was not limited to hydrolysis. With inorganic halides such as PCl_3 and BCl_3 , for instance, compounds of the type $(\text{CF}_3)_2\text{-NMCl}_2$ were not obtained; rather, the products were MF_3 , HCl and $\text{CF}_3\text{N}=\text{CCl}_2$. These may have been formed by the reactions.



Haszeldine has found previously that reactions 6 and 7 take place,⁹ and reaction 5 is well known. In a somewhat related reaction of I with CF_3COCI at 150° , HCl was identified in the forerun; however, no condensation to give $\text{CF}_3\text{CON}(\text{CF}_3)_2$ occurred, CF_3COF and $\text{CF}_3\text{N}=\text{CF}_2$ were probably formed, and the reaction was only 5% complete after 24 hours.

If elimination of HF can be avoided, more conventional reaction of the NH group can take place, and nitration by HNO_3 in CF_3COOH , under strictly anhydrous conditions, gave a fair yield of the nitramine $(\text{CF}_3)_2\text{N}\cdot\text{NO}_2$. Since hydrogen bonding and tautomerism are impossible, the compound was a colorless gas boiling at 17° , 170 degrees below the organic analog. It was stable toward aqueous alkali, but a sealed sample of the pure nitramine showed slow decomposition over several days at room temperature and the color of nitrogen oxides became apparent. The compound reacted readily with reducing agents but two factors—one, the marked tendency of an N-N bond toward cleavage, noted during reduction of aliphatic nitramines¹⁰ and probably increased by the large inductive effect of the trifluoromethyl groups, and two, the hydrolytic sensitivity of the $(\text{CF}_3)_2\text{N}-$ group—have prevented so far the detection of 1,1-bis-(trifluoromethyl)-hydrazine among the products. In the infrared spectrum of $(\text{CF}_3)_2\text{N}\cdot\text{NO}_2$, the N-O peak is found at 5.96μ ; this compares with 6.7 for $(\text{CH}_3)_2\text{N}\cdot\text{NO}$, 6.45 for $(\text{CF}_3\text{CH}_2)_2\text{N}\cdot\text{NO}$, 6.15 for $\text{C}_2\text{F}_5\text{-NO}_2$, and 5.47, 5.55 for the isomeric compound $(\text{CF}_3)_2\text{NONO}$, the dimer of CF_3NO .¹¹

Attempted nitrosation of I failed, either with sodium nitrite in CF_3COOH or with NOCl . This failure agrees with previous observations that the weaker amines are the more easily nitrated,¹⁰ and that the nitrosonium ion is less strongly electrophilic than the nitronium ion.¹²

(9) R. N. Haszeldine and D. A. Barr, Abstr. Amer. Chem. Soc. Meeting, Atlantic City, N. J., 1956, p. 13-M.

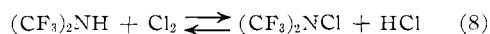
(10) A. H. Lambertson, *Quart. Repts.*, **5**, 75 (1951).

(11) R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 1741 (1957).

(12) Jack Hine, "Physical Organic Chemistry," McGraw-Hill Book Co. Inc., New York, N. Y., 1956, p. 133.

Because of the great ease of dehydrofluorination of I, metallic derivatives could not be made by conventional methods. The mercury derivative, however, could be obtained indirectly by reaction of II with mercuric fluoride. This reaction, which might be expected to lead to either $(\text{CF}_3)_2\text{NF}$ or $(\text{CF}_3)_2\text{N}-\text{N}(\text{CF}_3)_2$,¹³ resulted in an apparent addition of HgF_2 across the carbon-nitrogen double bond to give $(\text{CF}_3)_2\text{N}-\text{Hg}-\text{N}(\text{CF}_3)_2$. The formula proposed was substantiated by a single peak in the F^{19} nuclear magnetic resonance spectrum, indicating a symmetrical molecule with all fluorines equivalent, while the delta value of the peak indicated that the fluorines were present in the form of CF_3 groups. The mercurial was a heavy, colorless liquid, m.p. 17.5° , b.p. 127° , soluble in both fluorocarbon and hydrocarbon solvents. It was extremely sensitive to traces of moisture, hydrolyzing immediately with the formation of a yellow solid. When the compound was heated in glass above 150° , a colorless crystalline sublimate appeared which disappeared on cooling. Since the mercurial was completely recovered after this treatment, it would seem that the compound merely dissociated into II and mercuric fluoride, which recombined on cooling. No more than traces of permanent change were found at 300° .

Bromine did not react with I at temperatures as high as 200° . This lack of reaction is in agreement with Haszeldine's finding¹¹ that reaction 8 proceeds to the left rather than to the right at room temperature; in addition, it is likely that at 200° little

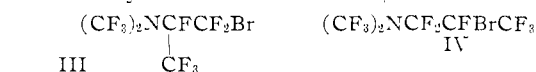


amine is present as such, the equilibrium $(\text{CF}_3)_2\text{NH} \rightleftharpoons \text{CF}_3\text{N}=\text{CF}_2 + \text{HF}$ lying to the right. N-Halogen derivatives could be made by indirect reaction, however. The mercury derivative reacted with bromine in carbon tetrachloride to give an excellent yield of $(\text{CF}_3)_2\text{NBr}$, b.p. 22° ; $(\text{CF}_3)_2\text{-NCl}$, b.p. -9° , was made similarly though not in good yield, and $(\text{CF}_3)_2\text{NF}$, b.p. -37° , was obtained through a different reaction.⁷ The N-bromo compound was stable in glass but quite reactive toward mercury, yielding HgBr_2 , $(\text{CF}_3)_2\text{N}-\text{Hg}-\text{N}(\text{CF}_3)_2$ and II. Coupling to form $(\text{CF}_3)_2\text{N}-\text{N}(\text{CF}_3)_2$, as suggested by Haszeldine,¹¹ was not observed. Infrared spectra in the series $(\text{CF}_3)_2\text{NBr}$, $(\text{CF}_3)_2\text{-NCl}$, $(\text{CF}_3)_2\text{NF}$ show some interesting changes as lines are progressively shifted toward shorter wave lengths. These are summarized in Table I.

TABLE I

PRINCIPAL INFRARED SPECTRAL LINES OF $(\text{CF}_3)_2\text{NX}$, μ	X	7.65	8.00	8.35	9.70	10.45	14.30
Br							
Cl		7.60	7.95	8.27	..	10.35	14.17
F		7.57	7.83	8.15	9.60	10.25	14.05

Addition of $(\text{CF}_3)_2\text{NBr}$ to $\text{CF}_3\text{CF}=\text{CF}_2$ took place readily at room temperature to give an adduct which may have been either III or IV. Although



(13) W. Hückel, *C. A.*, **44**, 4359 (1950); F. Nerdel, *Naturwiss.*, **39**, 209 (1952).

no rigorous proof of structure has been attempted, evidence from other addition reactions of $\text{CF}_3\text{CF}=\text{CF}_2^{11}$ strongly favors IV.

Experimental

$(\text{CF}_3)_2\text{NH}$.—Anhydrous HF (3.5 g.) and $\text{CF}_3\text{N}=\text{CF}_2$ (25 g.),¹⁶ were heated in an autoclave for 15 hours at 100° to give 27 g. (94%) of I, b.p. -6° , mol. wt. 153. Since the yield was acceptable, no study of conditions was made, although the reaction probably can be completed in a much shorter time.

Reaction with PCl_3 .—Fifteen grams (0.1 mole) of I and 14 g. of PCl_3 (0.1 mole) were heated in a stainless steel autoclave for four days at 100 – 140° . Fractionation of the product through a low temperature column gave 12.5 g. of overhead (Dry Ice–acetone condenser) and only one distillation flat, 9 g., b.p. 46° , mol. wt. 167. The mol. wt. for $\text{CF}_3\text{N}=\text{CCl}_2$ is 166, and an infrared spectrum showed strong C–N unsaturation at 5.62μ .

Anal. Calcd. for $\text{C}_2\text{Cl}_2\text{F}_3\text{N}$: Cl, 42.3. Found: Cl, 42.6.

The forerun reacted violently when bubbled through aqueous base, the resulting solution giving strong tests for F^- , Cl^- and, after oxidation, PO_4^{3-} . After the alkali had been exhausted, a small amount of gas passed through and was trapped in liquid air. This had mol. wt. 84, the mol. wt. of PF_3 being 88. The overhead before treatment with base had mol. wt. 57; an equimolar mixture of PF_3 and HCl has mol. wt. 62 and is the most probable combination of the observed acidic gases, b.p. below -80° , and containing P, Cl and F.

Reaction with BCl_3 .—Twelve and a half grams (0.08 mole) of I and 10 g. (0.08 mole) of BCl_3 were sealed in glass and heated at 110° for 15 hours. Fractionation gave 4 g. of I and 11 g. of $\text{CF}_3\text{N}=\text{CCl}_2$ (about 95% of theory), mol. wt. 166, b.p. 46° , infrared spectrum identical with that of a known sample. Seven grams of overhead was collected, very acidic, giving positive tests for boron and chlorine. The mol. wt. was 54, very close to the theoretical value, 52, for an equimolar mixture of BF_3 and HCl . An infrared spectrum showed the presence of BF_3 .

Reaction with CF_3COCl .—Ten grams of I (0.07 mole) and 17 g. of CF_3COCl (0.13 mole) were heated in a sealed glass tube for 24 hours at 100° . Fractionation returned 15 g. of CF_3COCl and 7.5 g. of I as unreacted starting materials. No material with a higher b.p. or mol. wt. than the original reactants was obtained; $\text{CF}_3\text{CON}(\text{CF}_3)_2$ would have b.p. 29° , mol. wt. 249.¹⁵ About 0.5 g. of HCl appeared as overhead and was trapped in liquid air; mol. wt. calcd. 37, found 37; chloride test positive. Fractional gram amounts were obtained at -57° and -37° to -27° , possibly CF_3COF , b.p. -60° , and I, b.p. -33° .

$(\text{CF}_3)_2\text{N}\cdot\text{NO}_2$.—Fifteen ml. of concd. HNO_3 (0.24 mole) was added to 150 g. of cold trifluoroacetic anhydride and the mixture stirred at 5° under a Dry Ice reflux condenser while 26 g. (0.17 mole) of I was slowly bubbled in. The condenser was then warmed to 25° and the reaction mixture heated to reflux. The crude nitramine passing overhead was trapped in Dry Ice, washed with water and dried with P_2O_5 , then stripped in a fractionating column to a temperature of 16° , the nitrogen oxides present as impurities either distilling over or solidifying on the Dry Ice head. The residue so obtained was colorless, boiled completely at 17° , and had mol. wt. 198, the theoretical value for $(\text{CF}_3)_2\text{N}\cdot\text{NO}_2$; yield 12 g., 43% of theory. A gas chromatogram showed better than 97% purity.

(14) J. D. LuZerte and R. J. Koslar, *THIS JOURNAL*, **77**, 910 (1955); M. Hauptschein, M. Braid and F. E. Lawlor, *ibid.*, **79**, 2549 (1957); R. J. Koslar, T. C. Simmons and F. W. Hoffmann, *ibid.*, **79**, 1741 (1957).

(15) Small quantities of this material are most conveniently prepared by heating $(\text{CF}_3)_2\text{NCOF}$ for 18 hours at 400° ; this gives a conversion of about 70% and quantitative yield. For large quantities a flow method is probably superior, cf. J. A. Young, T. C. Simmons and F. W. Hoffmann, *ibid.*, **78**, 5637 (1955).

Anal. Calcd. for $\text{C}_2\text{F}_6\text{N}_2\text{O}_2$: C, 12.1. Found: C, 12.2. The analyst reported "obvious nitrogen interference" in the value for fluorine.

$(\text{CF}_3)_2\text{N}\cdot\text{Hg}\cdot\text{N}(\text{CF}_3)_2$.—In a stainless steel autoclave, 52 g. of II (0.4 mole) and 50 g. of HgF_2 were heated for 15 hours at 100° . Five grams of II was recovered when the autoclave was opened *in vacuo*, and distillation of the residue gave 70 g. of $(\text{CF}_3)_2\text{N}\cdot\text{Hg}\cdot\text{N}(\text{CF}_3)_2$, b.p. 127° , m.p. 17.5° , or 79% of theory. The reaction yield is probably higher than this, but handling losses are considerable unless all operations on the mercurial are carried out in a perfectly dry atmosphere.

Anal. Calcd. for $\text{C}_4\text{F}_{12}\text{HgN}_2$: Hg, 39.8. Found: Hg, 39.8.

$(\text{CF}_3)_2\text{NBr}$.—A flask equipped with stirrer, addition funnel and short fractionating column was thoroughly dried by flaming under vacuum; 400 ml. of CCl_4 , distilled from P_2O_5 , was run in. One hundred twenty grams (0.24 mole) of $(\text{CF}_3)_2\text{N}\cdot\text{Hg}\cdot\text{N}(\text{CF}_3)_2$ was added, followed by 73 g. (0.46 mole) of bromine, previously distilled from P_2O_5 and dissolved in 200 ml. of dry CCl_4 . The bromine solution was added dropwise with stirring at room temperature. After about three-quarters of the bromine had been added decolorization became rather slow, and since free bromine was difficult to remove from the product, the reaction mixture was heated and the $(\text{CF}_3)_2\text{NBr}$ distilled off; 51 g. of light yellow liquid, b.p. 22° , was collected. The reaction was then continued at about 60° , the rest of the bromine added, and the product distilled off as it formed. In this way an additional 50 g., orange-red in color and containing a small amount of free bromine, was obtained. The total yield, 101 g., mol. wt. calcd. 232, found 232, represented 90% of theory. The N-bromo compound was very light yellow when pure and could be kept so indefinitely by sealing off together with a small amount of the mercury compound, but it very easily became contaminated by traces of free bromine, even during vacuum transfer if the system contained rubber tubing. Because of the difficulty in handling, no elemental analysis was made on the bromo compound itself, and reliance for proof of structure was placed upon the mol. wt., the method of synthesis, regeneration of the mercurial on treatment with mercury and analysis of the C_4F_8 adduct.

Reaction of $(\text{CF}_3)_2\text{NBr}$ with Mercury.—Two grams of $(\text{CF}_3)_2\text{NBr}$ was sealed in a glass tube with 1 g. of clean mercury and allowed to warm. Reaction took place at or below room temperature and considerable heat was liberated. After 15 hours, the tube was opened *in vacuo*. One gram of II, mol. wt. calcd. 133, found 133, completely absorbed by aqueous base, was transferred. A fraction of a gram was obtained of a liquid which transferred reluctantly in vacuum, had the characteristic odor of the mercurial, and reacted violently with water to give a yellow precipitate. This liquid was $(\text{CF}_3)_2\text{N}\cdot\text{Hg}\cdot\text{N}(\text{CF}_3)_2$. No traces of any volatile material with a mol. wt. approaching 304 ($(\text{CF}_3)_2\text{N}\cdot\text{N}(\text{CF}_3)_2$) and insensitive to water were detected.

Addition of $(\text{CF}_3)_2\text{NBr}$ to $\text{CF}_3\text{CF}=\text{CF}_2$.—Four grams of $(\text{CF}_3)_2\text{NBr}$ (0.017 mole) and 7 g. of C_3F_6 (0.05 mole) were sealed in a glass tube and heated at 100° for 24 hours, although this long a reaction period probably was not necessary since the reaction takes place readily at room temperature. Five grams of C_3F_6 , mol. wt. calcd. 150, found 148, was recovered, and distillation of the residue gave 4 g. of adduct, b.p. 84° , mol. wt. 382, found 384, n_D^{20} 1.2997, or 76% of theory. A gas chromatogram showed purity of 90% or better.

Anal. Calcd. for $\text{C}_5\text{F}_{12}\text{NBr}$: Br, 20.9; C, 15.7; F, 59.8. Found: Br, 20.7; C, 15.9; F, 59.8.

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