Chemistry of Nitrosyl Fluoride. I. Reactions of Nitrosyl Fluoride with Fluoro Ketones

S. ANDREADES

Contribution No. 776 from the Central Research Department,
Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware

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Nitrosyl fluoride reacts with certain fluoro ketones to give α-fluoronitrites, and nitryl fluoride adds similarly to hexafluorocyclobutanone to give heptafluorocyclobutyl nitrate, the first example of an α-fluoronitrate. Heptafluorocyclobutyl nitrite and nitrate readily rearrange to γ-nitroso- and γ-nitrohexafluorobutyryl fluoride, respectively. Excess aniline reacts with the above nitrite to form 1-(*p*-phenylazoanilino)hexafluorocyclobutan-1-ol. Mechanisms for the above reactions are proposed.

Since the initial synthesis of nitrosyl fluoride (I) in 1905,[1] its chemical behavior, particularly with organic compounds,[2] has been virtually ignored.[3] The infrared,[3d,e] microwave,[3f] near ultraviolet, and emission[3g] spectra, dipole moment,[3h] and heat of formation[3c] of nitrosyl fluoride have all been reported. Only one reaction with an organic substrate has been reported, that with benzene to give nitrobenzene.[3b] Recently, however, considerable interest in reactions of nitrosyl fluoride with fluoroölefins[2,4–6] has developed.

In this paper, reactions of nitrosyl fluoride with fluoro ketones to form new α-fluoronitrites, the first preparation of an α-fluoronitrate, and some novel chemistry associated with these compounds are described.

Preparation and Properties of Nitrosyl Fluoride. Nitrosyl fluoride is an extremely reactive gas whose properties make it imperative that dry,[7]

$$NOF + H_2O \longrightarrow HF + HONO$$

$$6NOF + SiO_2 \longrightarrow (NO)_2SiF_6 + 2NO + 2NO_2$$

inert reaction vessels be used. We found the use of glass[7] or stainless steel equipment intolerable.[2,3a–c] The acuteness of this situation made it necessary to ensure that the reaction examined truly involved I (and not the products of its reaction with the vessel[8] as reactants). In this respect, we found fluorinated[9] nickel, Monel, and Hastelloy "C" at elevated temperatures and "Teflon," TFE-fluorocarbon resin, or polyethylene equipment at moderate temperatures to be satisfactory.

Care must be taken in the choice of solvents used with nitrosyl fluoride. Solvents such as nitromethane, carbon tetrachloride, and benzene[10] are relatively inert at moderate temperatures. Compounds with active hydrogen liberate hydrogen fluoride,[11,12] and dimethylformamide reacts slowly with I at 20° to give dimethylnitrosamine, carbon monoxide, and hydrogen fluoride.

Nitrosyl fluoride has been prepared by the direct fluorination of nitric oxide,[3b,14] by the pyrolysis of a nitrosyl fluoroborate–sodium fluoride mixture,[3a,15] a nitrosyl hexafluoroantimonate–potassium fluoride mixture,[16] or a nitrosyl pyrosulfate–potassium fluoride mixture[17]; or by reaction of nitrosyl chloride with silver fluoride.[1] A new synthesis giving up to 80% yields has been found in the reaction of nitric oxide with excess silver difluoride[18] at 150°, but pressure equipment is required. Although direct fluorination[14] is an excellent method, we preferred the pyrolysis of nitrosyl fluoroborate–

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(1) O. Ruff and K. Stauber, *Z. anorg. allgem. Chem.*, **47**, 190 (1905).

(2) S. Andreades, Abstracts, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March, 1961, p. 26-O.

(3) The following papers deal mainly with spectral, inorganic, and physical chemical studies of nitrosyl fluoride. (a) G. Balz and E. Mailander, *Z. anorg. allgem. Chem.*, **217**, 161 (1934); (b) O. Ruff, W. Menzel, and W. Neumann, *ibid.*, **208**, 293 (1908); (c) H. S. Johnston and H. J. Bertin, Jr., *J. Am. Chem. Soc.*, **81**, 6402 (1959); (d) P. J. H. Woltz, E. A. Jones, and A. H. Nielsen, *J. Chem. Phys.*, **20**, 378 (1952); D. W. Magnuson, *ibid.*, **20**, 380 (1952); (e) E. A. Jones and P. J. H. Woltz, *ibid.*, 1516 (1950); (f) D. W. Magnuson, *Phys. Rev.*, **83**, 485 (1951); (g) H. S. Johnston and H. J. Bertin, *J. Mol. Spectr.*, **3**, 683 (1959); (h) D. W. Magnuson, *J. Chem. Phys.*, **19**, 1071 (1951); (i) D. Kawai and K. Shimiz, *Sci. Ind.* (Osaka), **29**, 9 (1955); (j) C. V. Stephenson and E. A. Jones, *J. Chem. Phys.*, **20**, 135 (1952); (k) A review of nitrosyl fluoride is included in C. J. Hoffman and R. G. Neville, "Nitrogen Fluorides and Their Organic Derivatives," *Chem. Rev.*, **62**, 1 (1962).

(4) S. Andreades, *J. Org. Chem.*, **27**, 4163 (1962).

(5) I. L. Knunyants, E. G. Bykhovskaya, V. N. Frosin, and Ya. M. Kisel, *Dokl. Akad. Nauk SSSR*, **132**, 123 (1960).

(6) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1151 (1960).

(7) The rapid reaction of nitrosyl fluoride with water or glass may be represented by the following equations[3a,b]

(8) In another paper,[4] it is pointed out that certain products obtained by other workers[5,6] undoubtedly arose *via* reaction of I with the reaction vessel followed by further reaction of the decomposition products (*e.g.*, NO_2) with the organic substrate.

(9) The surfaces of high nickel alloy metals are rendered particularly inert[3] due to formation of a coating of nickel fluoride according to the following exothermic reaction[3c]:

$$Ni + 2NOF \longrightarrow NiF_2 + 2NO$$

(10) No reaction occurred between nitrosyl fluoride and dry benzene at 25° and atmospheric pressure although reaction did occur[3b] at higher temperatures.

(11) An equilibrium is probably established, *i.e.*,

$$ROH + NOF \leftrightarrows RONO + HF$$

(12) Aromatic amines are diazotized by nitrosyl fluoride to give aryl fluoride and/or diazoamino compounds[13] directly.

(13) S. Andreades and A. Logothetis, unpublished results.

(14) A. V. Faloon and W. B. Kenna, *J. Am. Chem. Soc.*, **73**, 2937 (1951).

(15) E. Wilke-Dorfurt and G. Balz, *Z. anorg. allgem. Chem.*, **47**, 190 (1905).

(16) O. Ruff, K. Stauber, and H. Graf, *ibid.*, **58**, 325 (1908).

(17) G. A. Sokol'skii and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, No. **5**, 779 (1960).

(18) Dr. C. W. Tullock of these laboratories carried out initial work on this reaction. Nitryl fluoride can also be obtained by reaction of nitrogen dioxide with silver difluoride.

sodium fluoride mixtures for the laboratory preparation of large quantities of pure nitrosyl fluoride for several reasons. The use of large quantities of elemental fluorine is avoided, large supplies of the intermediate fluoroborate can conveniently be prepared and purified, and the product (whose purity depends on the purity of the intermediate) can be obtained pure directly in quantitative yields.

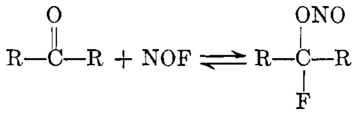
The preparation of nitrosyl fluoroborate[3a, 15, 19–23] was adapted from the literature.[19] Instead of an aqueous medium, if the reaction is run in dry nitromethane according to the following equation,

$$2NO_2 + HF + BF_3 \longrightarrow NOBF_4\downarrow + HNO_3$$

high yields of the anhydrous salt are obtained.

Results and Discussion

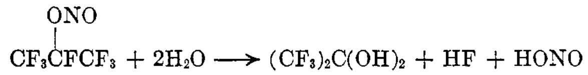
It has been found that an equilibrium is established rapidly at low temperatures between nitrosyl fluoride, fluoro ketone II and an α-fluoronitrite III.[24] The stability of the α-fluoronitrite is



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R + NOF \rightleftharpoons R{-}\underset{\underset{\displaystyle F}{|}}{\overset{\overset{\displaystyle ONO}{|}}{C}}{-}R$$

II III

markedly dependent on the nature of the R group and on temperature. Thus, when equimolar amounts of hexafluoroacetone (II, R = CF_3) and nitrosyl fluoride were combined at −195° and allowed to warm to 20°, immediate distillation gave a 95% yield of heptafluoroisopropyl nitrite[2] (III, R = CF_3). Hydrolysis of III proceeded vigorously to give hexafluoroacetone hydrate[5]:



$$CF_3\overset{\overset{\displaystyle ONO}{|}}{C}FCF_3 + 2H_2O \longrightarrow (CF_3)_2C(OH)_2 + HF + HONO$$

When the nitrite was heated (*ca.* 50°), nitrosyl fluoride was evolved and in glass equipment reacted to give $(NO)_2SiF_6$ (*vide supra*). The ketone was recovered. The infrared N=O stretching absorption of the nitrite appeared at 1840 $cm.^{-1}$,[25a] (vapor). The F^{19} n.m.r. spectrum at 56.4 Mc. showed a doublet at 210, 214 c.p.s. and a septet centered at 2855 c.p.s. (external reference: CF_3-COOH) with relative integrated intensities of *ca.* 6:1, respectively. The separation of the septet peaks was 4 c.p.s. The spectrum was consistent with a heptafluoroisopropyl compound with a coupling constant of 4 c.p.s. between α and β fluorine atoms.[26]

Addition of nitrosyl fluoride to tetradecafluoro-4-heptanone (II, R = n-C_3F_7) at 0°, on the other hand, gave a mixture which apparently had absorbed only one equivalent of nitrosyl fluoride and which showed nitrite infrared absorption. However, on warming to 20°, nitrosyl fluoride was evolved and starting ketone was recovered. α,α′-Dichlorotetrafluoroacetone gave a mixture which was *ca.* 70% nitrite and 30% ketone at 20° as estimated by F^{19} n.m.r. spectra. No primary nitrites were isolated when the method was attempted with perfluorinated acid fluorides.

The most stable nitrite encountered was heptafluorocyclobutyl nitrite (V, Fig. 1) which was prepared from hexafluorocyclobutanone (IV).[27] Similarly, it was found that nitryl fluoride[28] reacted rapidly at low temperatures to give high yields of heptafluorocyclobutyl nitrate (VII), the first example of a fluoroalkyl nitrate. Hydrolysis of V or VII gave hexafluorocyclobutanone hydrate (VI)[27] which is also accessible *via* the addition of

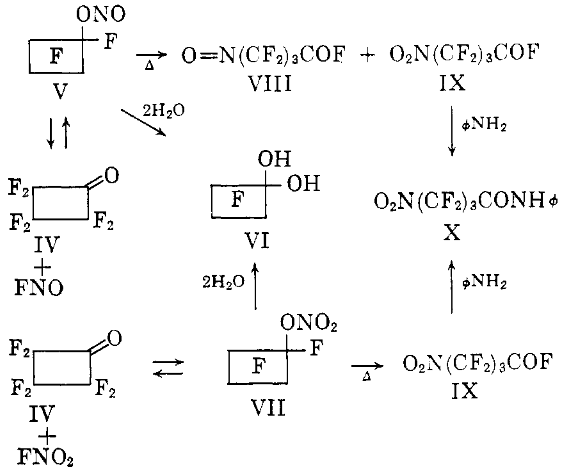


Figure 1

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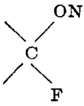
(19) S. A. Voznesenskii and P. P. Kurskii, *J. Gen. Chem. USSR*, **8**, 524 (1938).

(20) A. A. Woolf, *J. Chem. Soc.*, 1053 (1950).

(21) F. Seel, *Z. anorg. allgem. Chem.*, **250**, 331 (1943).

(22) M. Schmeisser, *Angew. Chem.*, **66**, 182 (1954).

(23) U. Wannagat and G. Hohlstein, *Chem. Ber.*, **88**, 1839 (1955).

(24) Structures containing the  function, until recently, have been unknown. *Cf.*, I. L. Knunyants and A. V. Fokin, *Bull. Acad. Sci. USSR*, **12**, 1462 (1957), and ref. 5.

(25) (a) The pronounced shift of the nitrite band to shorter wave lengths when substituted with an α-fluorine atom was found to be general. CF_3CH_2ONO (with β-fluorine atoms) absorbs at 1735 $cm.^{-1}$ while CH_3CH_2ONO absorbs at 1695 $cm.^{-1}$[25b]; (b) R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 4172 (1955).

(26) No rotational isomerism was evident at 20°. *Cf.* Nonfluorinated nitrites, W. D. Phillips in F. C. Nachod and W. D. Phillips, "Determination of Organic Structures by Physical Methods," Vol. 2, Academic Press, New York, N. Y., 1962, p. 442.

(27) D. C. England, *J. Am. Chem. Soc.*, **83**, 2205 (1961).

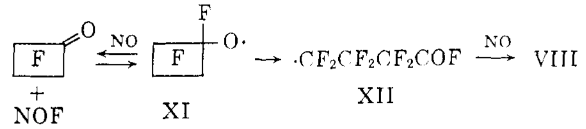
(28) Nitryl fluoride was prepared by the methods described in ref. 14 and 18 or by pyrolysis of NO_2BF_4 with sodium fluoride.[29] A convenient preparation of NO_2BF_4 was found in the reaction of hydrogen fluoride with fuming nitric acid in the presence of boron trifluoride. Addition of nitromethane to the resulting solution precipitated NO_2BF_4 in 48% yield, in agreement with S. J. Kuhn and G. A. Olah, *J. Am. Chem. Soc.*, **83**, 4564 (1961). This result is not in agrement with an earlier report[30] that $NOBF_4$ was obtained under similar conditions.

(29) M. Schmeisser and S. Elischer, *Z. Naturforsch.*, **7b**, 583 (1952); German Patent No. 918,506; *Angew. Chem.*, **66**, 182 (1954).

(30) R. Sprague, Abstracts, 134th National Meeting of the American Chemical Society, September, 1958, p. 2-S.

water to IV, or to heptafluorocyclobutanol,[31] the probable intermediate in the hydrolysis of V or VII.

The nitrite V when heated at 100° under autogenous pressure is rapidly rearranged to a mixture containing the deep blue[32a] γ-nitroso- (VIII) and γ-nitrohexafluorobutyryl fluoride (IX, Fig. 1). The same nitro acid fluoride IX is produced rapidly by gentle reflux of the nitrate VII.[32b] The identity of the nitro compound IX obtained from both reactions was further confirmed by conversion of each sample to the same anilide X.



XI XII

A common intermediate XI[33] is postulated for the conversions outlined in Fig. 1. Thus, this intermediate XI may lose a fluorine atom to nitric oxide produced from the cleavage to give NOF and ketone (reverse reaction of the equilibrium[35a]) or it may rearrange to the ring opened radical XII which gives product VIII by reaction with nitric oxide.[35b] The nitro acid fluoride IX could arise by reaction of radical XII with nitrogen dioxide (produced in the nitrate decomposition or from disproportionation of NO[35c]) or by oxidation[32a] of VIII by NOF or NO from the nitrite decomposition. Only small amounts of IX were produced from V.

Reaction of V with excess aniline gave exothermically an 80% yield of 1-[p-(phenylazo)anilino]-hexafluorocyclobutan-1-ol (XIII), probably *via* the intermediates[36] suggested in Fig. 2. The structure of XIII was confirmed by its synthesis from p-(phenylazo)aniline and IV in 84% yield.[36] Treatment of XIII with cold alcoholic potassium hydroxide gave the rearranged butyranilide XIV.[36a]

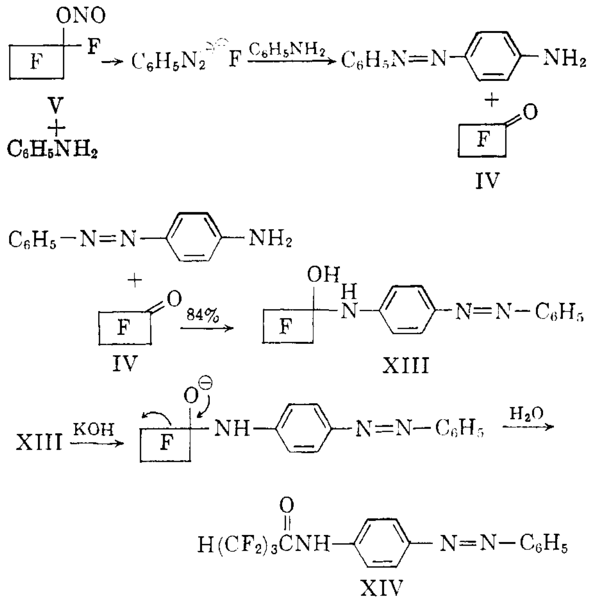
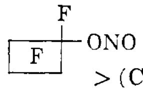


Figure 2

Reactivity of Fluoro Ketones.—Qualitatively, the order of stability of the nitrites appears to be:



$$> (CF_3)_2CFONO > (R_fCF_2)_2CFONO > R_fCF_2ONO$$

Apparently, there is a great tendency for the carbonyl carbon in IV to be converted to an sp^3 tetrahedral configuration in spite of the apparently adverse steric situation. This reactivity of IV probably stems partly from the concomitant conversion of the partially positive carbonyl carbon (a highly unfavorable circumstance in view of the adjacent electronegative —CF₂— groups) to a saturated state not requiring a fractional positive charge. Indeed, that the contribution of the ionic resonance extreme $(\overset{\diagdown\oplus}{\underset{/}{C}}—O^{\ominus})$ is greatly decreased in IV as compared to normal ketones is clearly indicated by the shift of the carbonyl stretching frequency in IV to the highest value recorded for a ketone[2, 27] (1850 cm.$^{-1}$ compared to *ca.* 1700 cm.$^{-1}$ for normal ketones or *ca.* 1780 cm.$^{-1}$ for open-chain fluoroketones). Consequently, addition reactions of even acidic reagents with fluoro ketones most likely proceed *via* initial attack of the anionic portion of the substrate[2, 37] (in this case, fluoride ion) so that in the transition state, the organic moiety

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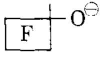
[31] S. Andreades and D. C. England, *J. Am. Chem. Soc.*, **83**, 4670 (1961).

[32] (a) Compounds containing the CF₂N=O function are stable in the monomeric state and, therefore, are an intense blue. See, *e.g.*, R. N. Haszeldine, *J. Chem. Soc.*, 2075 (1953); (b) Several explosions occurred when VII was heated under pressure. Rearrangement of VII occurred slowly even at 20°.

[33] Alternatively, an ionic mechanism involving



is possible, but radical cleavage of the nitrite[34] (or nitrate) seems more likely particularly in view of the vapor phase conditions and the general assumption[34] that thermal decomposition of alkyl nitrites proceeds homolytically as shown to sever the weakest (O—N) bond.

[34] B. C. Gowenlock and J. Trotman, *J. Chem. Soc.*, 4190 (1955); 1670 (1956); P. Gray, *Trans. Faraday Soc.*, **51**, 1367 (1955); See also E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. I. Reinhold Publishing Corp., New York, N. Y., 1954, p. 239; P. Gray, P. Rathbone, and A. H. Williams, *J. Chem. Soc.*, 3932 (1960).

[35] (a) By the principle of microscopic reversibility, the addition of I to IV must proceed through XI in the vapor phase reaction. That the addition is free radical in nature in the vapor phase is not incompatible with the postulate of an ionic mechanism for the same reaction at low temperatures in the condensed phase; (b) The questions of whether this is a chain or an intramolecular process and the identity of the other products have not been investigated; (c) J. F. Brown, *J. Am. Chem. Soc.*, **79**, 2480 (1957).

[36] Aniline reacts with IV to give a similar addition product which also rearranges on treatment with base to give the corresponding ring-opened product. Another possible mechanism which does not require diazotization involves displacement of fluoride ion in V by aniline, rearrangement of the resulting nitrite to 1-(p-nitrosoanilino)-hexafluorocyclobutan-1-ol in several steps, and subsequent condensation of the nitroso compound with aniline to give XIII.

[37] This situation is identical to that which must apply in the additions of HX to IV.[31]

has oxyanion character rather than oxonium or carbonium ion character encountered in the protonation of normal ketones in acid solution.[38]

That there is an added factor contributing to the reactivity of IV is shown by the greater stability of V, VI, and heptafluorocyclobutanol[31] compared to the corresponding open-chain compounds.[39] Hence, the relief of bond angle distortion[39b] effected by conversion of IV to a cyclobutyl derivative is probably a second major factor. The carbonyl stretching frequencies of IV, 1855 cm.$^{-1}$; cyclobutanone, 1775 cm.$^{-1}$; hexafluoroacetone, 1815 cm.$^{-1}$; and acetone, 1745 cm.$^{-1}$; support the above views.

Infrared Spectrum of Heptafluorocyclobutyl Nitrite.—Normal alkyl nitrites display N=O stretching as a doublet with the higher frequency peak much more intense than the other. For example, *n*-butyl nitrite shows absorption at 1670 cm.$^{-1}$ (strong) and 1613 cm.$^{-1}$ (moderate). The occurrence of two peaks has been interpreted in terms of *cis–trans* rotational isomerism,[25b, 40] the higher energy peak being assigned to the *trans* rotational isomer. In 2,2,2-trifluoroethyl nitrite, the ratio of *trans* isomer (1740 cm.$^{-1}$) to *cis* (1696 cm.$^{-1}$) appears to increase. This trend toward higher frequencies and greater proportions of the *trans* isomer as fluorine substitution is increased or moved closer to the nitrite function is followed in V which has an intense peak at 1860 cm.$^{-1}$ and a very weak band at 1750 cm.$^{-1}$. The *cis–trans* isomerization at 20° is apparently too rapid to observe by n.m.r.[26]

Experimental[41]

Nitrosyl Fluoroborate.[42]—A polyethylene reactor arranged for stirring and containing 900 ml. of dry nitromethane was equipped with a gas inlet tube extending below the surface of the liquid, and an exit tube leading to a T-tube through which was passed a slow stream of dry nitrogen. The reactor was cooled to −20° with stirring and 60 g. (3.0 moles) of anhydrous hydrogen fluoride, 204 g. (3.0 moles) of boron trifluoride and 276 g. (6.0 moles) of nitrogen dioxide were each added slowly in that order. The rate of addition of each reagent was controlled so that the temperature was maintained below 0°. During the addition of nitrogen dioxide, precipitation of the fluoroborate occurred. The white precipitate was collected by filtration in a drybox, washed successively with three 75-ml. portions of nitromethane and three 75-ml. portions of carbon tetrachloride, and dried overnight in a heated (50–100°) vacuum desiccator. The yield was 341 g. (97%). An analytical sample was purified further by sublimation.

Anal. Calcd. for $NOBF_4$: F, 65.1; N, 12.0; BF_4,[43] 74.3. Found: F, 65.0; N, 11.7; BF_4, 74.1.

That NO_2BF_4 was not a contaminant was shown by the fact that the product was inert to benzene[44] at 20°, and that pure NOF was obtained directly in the next experiment.

Nitrosyl Fluoride (I).—In a drybox, 117 g. (1.0 mole) of dry nitrosyl fluoroborate and 84 g. (2.0 moles) of dry sodium fluoride were mixed intimately and placed in a 300-ml. perfluorinated Monel reactor. Nickel tubing (with a T-joint and a Monel Hoke valve leading to a vacuum pump) was connected from the reactor to a 300-ml. Monel cylinder which served as a receiver. Both reactor and receiver were equipped with safety rupture discs. The entire system was evacuated while heating the reactor to *ca.* 80°. The Hoke valve was then closed, the receiver was cooled in liquid nitrogen, and the reactor was heated at 250° for 6 hr. After allowing the reactor to cool, the system was evacuated to *ca.* 0.15 mm. and the receiver cylinder was closed and allowed to warm to room temperature. The yield was 48.5 g. (99%) of pure nitrosyl fluoride.

Anal. Calcd. for NOF: F, 38.78. Found: F, 38.71, 38.72, 38.67.

The infrared spectrum of this material was taken in a prefluorinated Monel gas cell with calcium fluoride or silver chloride windows. At most, only very small amounts of nitrogen dioxide and, occasionally, traces of nitrous oxide were observed as impurities when suitable precautions were taken both in the preparation and during sampling. The central components of the intense triplets occurred at 1850 and 767 cm.$^{-1}$.[3d,e]

Nitryl Fluoroborate.—Nitryl fluoroborate was obtained by the methods described.[28,29] The hygroscopic material obtained from the first method[28] was identified by its vigorous reaction with benzene to give nitrobenzene,[44] by its pyrolysis with sodium fluoride to give pure nitryl fluoride[28,29] (next experiment) and by elemental analysis.

Anal. Calcd. for NO_2BF_4: F, 57.2. Found: F, 57.1.

When nitromethane was added to the nitric acid solution of boron trifluoride before the addition of hydrogen fluoride, no precipitation occurred. If hydrogen fluoride was then added, precipitation of the product occurred.

Nitryl Fluoride.[18,28,29]—The pyrolysis[28] was conducted in the manner described for nitrosyl fluoride. The identity of the nitryl fluoride was established by its infrared spectrum,[45] its reaction with boron trifluoride[46] in nitromethane to give nitryl fluoroborate, and its rapid reaction with benzene to give nitrobenzene.[47]

Heptafluoroisopropyl Nitrite.—Into a dry, evacuated 30-ml. Monel vessel which was cooled in liquid nitrogen was distilled *in vacuo* 10.5 g. (0.063 mole) of hexafluoroacetone and 3.0 g. (0.061 mole) of nitrosyl fluoride. The reactor

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(38) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, chap. XI.

(39) (a) For additional discussion of fluoroketone hydrates, see H. E. Simmons and D. W. Wiley, *J. Am. Chem. Soc.*, **82**, 2288 (1960); (b) L. L. Ingraham in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1956, p. 506.

(40) (a) P. Tarte, *J. Chem. Phys.*, **20**, 1570 (1952); (b) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958, p. 304.

(41) Boiling points and melting points are uncorrected. N.m.r. spectra were taken on a Varian Associates 60-Mc. high resolution n.m.r. spectrometer. Infrared spectra were taken on a Perkin–Elmer Model 21 spectrophotometer, ultraviolet spectra on a Cary Model 14 spectrometer, and mass spectra on a Consolidated Electrodynamics Corp. Model 21-103C mass spectrometer using a room temperature inlet, an ionizing potential of 70 e.v. and an ionizing current of 10.5 μamp. All experiments involving nitrosyl or nitryl fluoride were carried out using prefluorinated nickel, Monel, Hastelloy C, "Teflon," TFE-fluorocarbon resin, or polyethylene equipment. Closed metal reactors were equipped with safety disks set to rupture at an appropriate pressure. Manometers and flowmeters were fabricated from polychlorotrifluoroethylene tubing, or Monel. Mercury surfaces were covered with a layer of Halocarbon Oil (Halocarbon Products Corp., Hackensack, New Jersey). Low temperature distillations were carried out in low temperature stills packed with Hastelloy "C" Heli-pak (Podbielniak, Inc., Chicago, Ill.).

(42) Recently, it was announced that NOF and $NOBF_4$ can be purchased from the Ozark-Mahoning Co., Tulsa, Okla.

(43) W. Lange, *Ber.*, **59**, 2107, 2432 (1926).

(44) NO_2BF_4 reacts vigorously with benzene to give nitrobenzene, G. Olah, S. Kuhn, and A. Mlinkó, *J. Chem. Soc.*, 4257 (1956).

(45) R. E. Dodd, J. A. Rolfe, and L. A. Woodward, *Trans. Faraday Soc.*, **52**, 145 (1955).

(46) G. Hetherington and P. L. Robinson, *Chem. Soc.* (London) *Spec. Publ.*, **10**, 23 (1957); E. E. Aynsley, G. Hetherington, and P. L. Robinson, *J. Chem. Soc.*, 1119 (1954).

(47) G. Hetherington and P. L. Robinson, *ibid.*, 3512 (1954).

was closed and allowed to warm to room temperature. Distillation yielded 2.6 g., b.p. 5–26°, and 11.8 g. (90%) of light yellow heptafluoroisopropyl nitrite, b.p. 27–28°. The nitrite was extremely reactive and moisture-sensitive and analyses were obtained on samples in sealed vials cooled in Dry Ice before opening under dry nitrogen.

Anal. Calcd. for $C_3F_7NO_2$: F, 61.9. Found: F, 62.2.

The infrared spectrum showed strong ON=O stretching absorption at 1840 cm.$^{-1}$. The F^{19} n.m.r. spectrum is described above.

Hydrolysis of Heptafluoroisopropyl Nitrite.—Addition of the nitrite to an equivalent amount of water gave a vigorous reaction with the evolution of brown fumes. The resulting hexafluoroacetone hydrate, b.p. 110–114°, was identified by comparison of its infrared spectrum with that of an authentic sample and by conversion to hexafluoroacetone semicarbazone,[48] m.p. 149–151°.

Heptafluorocyclobutyl Nitrite (V).—This preparation and the elemental analyses were carried out as described for heptafluoroisopropyl nitrite. From 48.0 g. (0.27 mole) of hexafluorocyclobutanone and 13.0 g. (0.26 mole) of nitrosyl fluoride in an 80-ml. Monel reactor was obtained 56.5 g. (96%) of V, b.p. 55° (some dec.); or 7° (105 mm.), as a yellow, moisture-sensitive liquid.

Anal. Calcd. for $C_4F_7NO_2$: C, 21.16; F, 58.59; N, 6.17; mol. wt., 227.04. Found: C, 21.25; F, 58.75; N, 5.98; mol. wt., 228 (f.p. in benzene).

The ultraviolet spectrum[49] of V in isoöctane showed a λ_{max} at 348 mμ (ϵ 60) and end absorption at 210 mμ (ϵ 1000). The infrared spectrum of V is discussed above.

The F^{19} n.m.r. spectrum at 56.4 Mc. showed a four line AB multiplet (four β-fluorines) and two single bands (two γ and one α fluorine) with approximate integrated intensity ratios of 4:2:1, respectively. The AB bands appeared at 2752, 2974, 3088, 3312 c.p.s.; the γ-fluorine band at 3263 c.p.s.; and the α-fluorine band at 2804 c.p.s., all externally referenced from trifluoroacetic acid at 56.4 Mc.

Hexafluorocyclobutanone Hydrate (VI).[27]—To 14.5 g. (0.064 mole) of V was added dropwise 2.5 g. (0.139 mole) of water. A vigorous reaction ensued accompanied by the evolution of brown fumes. Distillation of the product gave an 86% yield of VI, b.p. 126–130°, m.p. 55–57°. Infrared spectra of this material and of an authentic sample were identical.

Heptafluorocyclobutyl Nitrate (VII).—In the same manner described for the preparation of V, 19.0 g. (0.106 mole) of hexafluorocyclobutanone and 7.0 g. (0.107 mole) of nitryl fluoride gave 23.0 g. (89%) of VII, b.p. 16–18° (120 mm.). The nitrate was extremely sensitive to heat and atmospheric moisture making it difficult to obtain good analytical values.

Anal. Calcd. for $C_4F_7NO_3$: F, 54.7; N, 5.8; mol. wt., 243.0. Found: F, 55.0; N, 5.5; mol. wt., 243 (f.p. in benzene).

The strong α-fluoronitrate infrared absorption occurred at 1740 cm.$^{-1}$ (asymmetric ONO_2 stretching) and at 1410 cm.$^{-1}$ tentatively assigned to the symmetric ONO_2 stretching. The F^{19} n.m.r. spectrum at 56.4 Mc. showed three peaks at 3035, 3149 and 3547 c.p.s. relative to trifluoroacetic acid (external reference) with relative integrated intensities of 4(β-fluorines), 2(γ-fluorines) and 1(α-fluorine), respectively.

γ-Nitrohexafluorobutyryl Fluoride (IX).—Ten grams of VII was refluxed in a Pyrex flask for 1 hr. Considerable material was lost due to reversion back to ketone IV and nitryl fluoride. Heating in a closed pressure vessel was avoided because of repeated explosions. Distillation gave 2.5 g. (25%) of IX, b.p. 55–60°. A sample of IX reacted with water, and the resulting mixture gave a positive test for fluoride ion. The infrared spectrum of IX showed peaks at 1890 cm.$^{-1}$ (strong, —$\overset{O}{\overset{\|}{C}}$—F), and 1622 cm.$^{-1}$ (strong, —CF_2NO_2).[50] Only small amounts of starting material were present as an impurity. The F^{19} n.m.r. spectrum (40 Mc.) displayed peaks at −4010 (—$\overset{O}{\overset{\|}{C}}$—F), 865, 1696, and 1859 c.p.s. (three —CF_2— resonances) relative to trifluoroacetic acid (external reference) with relative areas 1:2:2:2, respectively.

γ-Nitrohexafluorobutyranilide (X).—This derivative of IX was prepared by adding a small sample to excess aniline. The resulting anilide X was recrystallized from heptane as needles, m.p. 82–82.5°.

Anal. Calcd. for $C_{10}H_6F_6N_2O_3$: C, 38.00; H, 1.91; N, 8.87; mol. wt., 316.10. Found: C, 38.13; H, 2.08; N, 8.58; mol. wt., 313 (b.p. in ethylene chloride).

The infrared spectrum of X had bands at 3280 cm.$^{-1}$ (N—H), 3080 (aromatic C—H), 1710 ($\overset{O}{\overset{\|}{C}}$—N), 1600 (—$NO_2$ and aromatic C=C), 1550 (N—H deformation, amide II band[40b]), 1505 (aromatic), 1332 (NO_2) and broad C—F absorption in the 1150-cm.$^{-1}$ region. The F^{19} n.m.r. spectrum (56.4 Mc.) in chloroform had only three equally intense —CF_2— peaks at 1040, 2270, and 2470 c.p.s. relative to trifluoroacetic acid (external reference).

γ-Nitrosohexafluorobutyryl Fluoride (VIII) from Rearrangement of V.—Into a 100-ml. Monel pressure vessel was distilled *in vacuo* 39.0 g. (0.17 mole) of V. The vessel was closed and heated at 100° for 0.5 hr. Distillation of the liquid products gave fraction 1, b.p. 4° (270 mm.), 1.5 ml. (deep blue[32a,50]), fraction 2, b.p. 4–21° (270 mm.), 3.5 ml. (deep blue-green); and fraction 3, b.p. 21–27° (270 mm.), 15 g. (yellow). The remaining mixture boiled up to 130° (260 mm.). Fraction 3 was mainly V but contained some IX. Fractions 1 and 2 were cooled in Dry Ice in a dry box in order to freeze the nitrogen dioxide impurity. Filtration at −80° and distillation of the filtrate gave 6.0 g. (25% taking into account the recovered starting material) of VIII, b.p. 26–30° (deep blue) and 1.00 g. of IX, b.p. 55–60°, which had an infrared spectrum identical with the IX described above and was converted to the same anilide X, m.p. 81.5–82.5°. This anilide had an infrared spectrum identical to the spectrum of X described above.

The F^{19} n.m.r. spectrum of VIII (40 Mc.) had signals at −3982 (—$\overset{O}{\overset{\|}{C}}$—F), 1550, 1708, and 1950 c.p.s. (three —CF_2— groups) relative to trifluoroacetic acid (external reference) with relative areas of 1:2:2:2, respectively. Three small impurity bands (CF_3) were noticed. The infrared spectrum of VIII showed peaks at 1890 cm.$^{-1}$ (—$\overset{O}{\overset{\|}{C}}$—F), 1630 cm.$^{-1}$, ($CF_2$—N=O),[50] and broad C—F absorption in the 1200 cm.$^{-1}$ region.

When a sample of VIII was treated with water, a blue aqueous solution was obtained which gave a positive test for fluoride ion. Since VIII was only moderately stable,[4] it was sealed under nitrogen and stored at −80° until used. Contamination by IX, $ON(CF_2)_4ONO$, or $ONO(CF_2)_3COF$ was suspected.

Vapor phase chromatography of VIII was carried out on a 12 ft. × $^1/_4$ in. o.d. copper column packed with 20% w./w. ethyl ester of Kel-F Acid No. 8114 (Minnesota Mining and Manufacturing Co.) supported on 40–60 mesh "Columpak" (Fisher Scientific Co.) maintained at 0° with a helium flow rate of 60 cc./min. The retention time of VIII under these conditions was 19.9 min. The main

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(48) A. L. Henne, J. W. Shepard, and E. J. Young, *J. Am. Chem. Soc.*, **72**, 3577 (1950).

(49) *n*-Butyl nitrite in petroleum ether has λ_{max} 356 mμ (ϵ 87), and 222 (ϵ 1700), while 2,2,2-trifluoroethyl nitrite vapor has a λ_{max} at 364 mμ.[25b]

(50) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 3416 (1956).

impurity believed to be the nitrite, $ONO(CF_2)_3COF$, was colorless, evolved NOF readily, and eluted at 13.2 min. The 19.9-min. peak was isolated and had the same n.m.r. spectrum as described above, but the impurity bands were absent.

Anal. Calcd. for $C_4F_7O_2N$: F, 58.6; N, 6.2; mol. wt., 227.04. Found: F, 58.7; N, 6.6; mol. wt., 217 (Victor Meyer). A micro boiling point determination by differential thermal analysis gave a value of 31°.

The *m/e* values in the mass spectrum[41] of VIII isolated from vapor phase chromatography are tabulated below. The highest mass peak was the low yield *m/e* 197 fragment (parent—NO) and no parent ion was seen. No other ion less than 1% of the most abundant *m/e* 30 (NO^+) is included.

m/e	Relative abundance, %	Ion
197	2.9	$C_4F_7O^+$
169	22.4	$C_3F_7^{+a}$
150	2.3	$C_3F_6^+$
131	11.5	$C_3F_5^+$
128	1.5	$C_3F_4O^+$
119	18.0	$C_2F_5^{+a}$
109	1.3	$C_3F_3O^+$
100	24.0	$C_2F_4^+$
97	1.4	$C_2F_3O^+$
93	1.9	$C_3F_3^+$
81	1.9	$C_2F_3^+$
80	1.5	CF_2NO^+
69	75.0	CF_3^{+a}
62	1.4	$C_2F_2^+$
50	7.9	CF_2^+
47	15.2	COF^+
31	28.5	CF^+
30	100.0	NO^+

[a] Rearrangement ions.

The absence of a parent ion in the mass spectrum of VIII is not surprising in view of the extremely low abundance or absence of parent ions from other nitrosoperfluoroalkanes in a similar molecular weight range run under similar conditions in this laboratory [4,51] The appearance of the *m/e* 30 (NO^+) as the most abundant ion is consistent with the nitrosofluorocarbon structure.[4,51] The rearrangement ion $(CF_3)^+$ is also expected,[52] particularly from a perfluoroacyl fluoride. Similarly, a $C_2F_5^+$ rearrangement peak is normal[52] and probably arises *via* loss of CO from an acyl fluoride fragment. The absence of a *m/e* 46 ion (NO_2) is consistent with the absence of a nitrite or nitro function. A molecular weight of 227 ($C_4F_7O^+ + NO^+$) may be deduced from the data.

Reaction of V with Aniline.—To a solution of 20.0 g. (0.215 mole) of aniline in 50 ml. of ether cooled to 0° was added slowly with stirring 15.0 g. (0.066 mole) of V. Filtration gave 24.0 g. (100%) of crude solid XIII. Recrystallization three times from large volumes of hexane gave an 80% yield of XIII, m.p. 143–145°.

Anal. Calcd. for $C_{16}H_{11}F_6N_3O$: C, 51.20; H, 2.95; N, 11.20; F, 30.38; mol. wt., 375.29. Found: C, 50.92; H, 2.84; N, 11.27; F, 30.39; mol. wt. 376 (b.p. in ethylene chloride).

The infrared spectrum showed absorption in the 3390 cm.$^{-1}$ region (N—H) and (O—H), and no amide carbonyl absorption either in the solid state or in acetonitrile solution. The ultraviolet spectrum (ethanol) had λ_{max} 250 mμ (ϵ 8440) and at 384 mμ (ϵ 21,000). The F^{19} n.m.r. spectrum in chloroform at 40 Mc. showed two peaks of relative areas 2:1 indicating the cyclobutane ring was still intact. A H^1 n.m.r. spectrum (60 Mc.) in chloroform-*d* showed two aromatic hydrogen signals of relative weights 5:4 and two other peaks each of relative weight 1, assigned to NH and OH. The properties and spectra of this material were identical with those of XIII synthesized independently in the next experiment.

1-[*p*-(Phenylazo)anilino]hexafluorocyclobutan-1-ol (XIII).—To a solution of 6.0 g. (0.034 mole) of IV in 50 ml. of chloroform cooled in an ice bath was added with stirring a solution of 5.0 g. (0.025 mole) of *p*-phenylazoaniline in 50 ml. of chloroform. Evaporation of the chloroform with a stream of nitrogen left a bright yellow solid which was recrystallized from 1.5 l. of hexane to give 8.0 g. (84%) of XIII as orange-yellow needles, m.p. 144–146°. The product had an infrared spectrum identical to that of the material (XIII) obtained in the previous experiment.

Base-catalyzed Rearrangement of XIII to 2,2,3,3,4,4-Hexafluoro-4′-(phenylazo)butyranilide (XIV).—In 10 ml. of ethanol was dissolved 0.50 g. of XIII, and 1.0 ml. of 10% sodium hydroxide solution was added. The mixture was acidified with dilute hydrochloric acid. The precipitate was collected by filtration and washed with several portions of water to give yellow crystals which were recrystallized from hexane to give 0.46 g. (92%) of XIV, m.p. 134–135°. The infrared spectrum showed strong amide carbonyl absorption at 1720 cm.$^{-1}$. The F^{19} n.m.r. spectrum (40 Mc.) in acetone showed three —CF_2— peaks with equal integrated intensities.

Anal. Calcd. for $C_{16}H_{11}F_6N_3O$: C, 51.20; H, 2.96; F, 30.38; N, 11.20. Found: C, 51.29; H, 3.01; F, 30.37; N, 11.43.

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[51] See also V. A. Ginsburg, N. F. Privezentseva, V. A. Shpanskii, N. P. Rodinova, S. S. Dubov, A. M. Khokhlova, S. P. Makarov, and A. Yas Yakubovich, *J. Gen. Chem. USSR*, **30**, 2391 (1960).

[52] J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960, p. 413; F. W. McLafferty, in ref. 26, p. 151, 165; F. L. Mohler, V. H. Dibeler, and R. M. Reese, *J. Res. Natl. Bur. Std.*, **49**, 343 (1952).