Chemistry of Nitrosyl Fluoride. II. Reactions of Nitrosyl Fluoride with Fluoroölefins[1]

S. ANDREADES

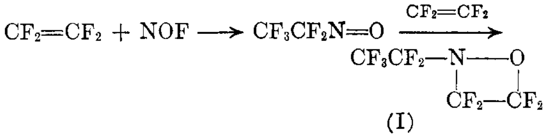
Contribution No. 777 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware

Received July 5, 1962

Reactions of nitrosyl fluoride with tetrafluoroethylene, hexafluoropropene, octafluoroisobutene, and octafluoro-2-butene to give oxazetidines, nitroso compounds, and/or azaalkenes are described. A rationalization of relative reactivities of and direction of addition to fluoroölefins is presented. Detailed studies of the nitrosyl fluoride–hexafluoropropene reaction led to a new synthesis of perfluoroazaalkenes. Thermal decomposition of nitrosoperfluoroalkanes gives perfluoroazaalkenes, nitrites, nitro compounds, and nitrosyl fluoride. Both nitrosyl and nitryl fluoride add readily to pentafluoroazapropene to form N-nitroso- and N-nitrobis(trifluoromethyl)amine, respectively. Mechanisms of the various reactions and factors affecting oxazetidine formation are discussed. The temperature dependence of the F^{19} n.m.r. spectra of the N-nitrosoamine, a perfluoroazaalkene, and an oxazetidine indicate considerably smaller barriers to rotation in the first system or inversion in the latter two materials compared to similar nonfluorinated systems.

Reaction of nitrosyl fluoride with organic compounds has received little attention[1,2] although this extremely reactive gas was reported in 1905.[3] In the present paper, we wish to report studies of reactions of nitrosyl fluoride with some fluoroölefins and azaalkenes and to describe some related chemistry of nitrosofluorocarbons which are directly involved as intermediates in these reactions.

In contrast to the very facile additions to fluoroketones[1,2] and pentafluoroazapropene[1] at low temperatures, addition of nitrosyl fluoride to tetrafluoroethylene and hexafluoropropene required relatively high temperatures and pressures. Thus, when two equivalents of tetrafluoroethylene and one equivalent of nitrosyl fluoride were heated at 100° in a prefluorinated Hastelloy "C" vessel,[4] the autogenous pressure decreased from 1120 p.s.i.g. to 260 p.s.i.g. in eight hours, and a 55% yield of 2-pentafluoroethyl-3,3,4,4-tetrafluoro-1,2-oxazetidine (I) was obtained according to the following sequence



(1)

(I)

The initial addition of nitrosyl fluoride to fluoroölefin must be rate-determining since more than trace amounts of the intermediate nitrosoethane cannot be isolated even if a large excess of nitrosyl fluoride is used. Furthermore, it has been shown that the succeeding step (the four-center reaction of a primary nitrosofluorocarbon with tetrafluoroethylene) occurs readily at low temperatures[5] in the absence of light. When the above reaction was carried out at 200°, mainly carbonyl fluoride and heptafluoro-2-aza-1-butene were obtained due to cleavage of I, probably *via* initial rupture of the N—O bond.[5] This characteristic decomposition pattern of fluoroalkyl oxazetidines has been used as chemical evidence for the structures.[5]

Recently, two other independent reports concerning the reaction of nitrosyl fluoride with tetrafluoroethylene[6,7a] and with other fluoroölefins[6] have appeared. Both [6,7a] report the formation of I, but Knunyants, *et al.*,[6] do not report a yield, used steel (composition unspecified) tubes, and state that in the absence of a charcoal–calcium sulfate catalyst, other products are obtained. Barr and Haszeldine[7a] obtained 13% of I[7b] after conducting the reaction in glass, which is known[2,4] to react with nitrosyl fluoride to give nitrogen dioxide and nitric oxide. Indeed, the bulk of their[7a] products ($CF_2NO_2CF_2NO_2$ and CF_2NO_2-COF) undoubtedly arose from reaction of the olefin with nitrogen dioxide,[8] since the addition of nitrogen dioxide to tetrafluoroethylene has been shown previously to give these two products.[8] The CF_2NO_2COF would be formed readily by loss of nitrosyl fluoride from $CF_2NO_2CF_2ONO$.[9] We obtained very small amounts of these side products,[10] found Type 316 stainless steel vessels unsatisfactory, and avoided the use of complicating catalyst systems.

---

[1] This work was presented in part at the 139th National Meeting of the American Chemical Society, St. Louis, Mo., March, 1961, p. 26-O of the Abstracts.

[2] S. Andreades, *J. Org. Chem.*, **27**, 4157 (1962). The literature on nitrosyl fluoride is reviewed in this paper.

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

[4] The necessity of using dry, inert reaction vessels was emphasized in the previous paper.[1,2] The use of glass, particularly, *must* be avoided if the reaction examined is to involve nitrosyl fluoride rather than products of its reaction with the vessel[2] (*vide infra*).

[5] See, for example (a) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1881 (1955); (b) D. A. Barr and R. N. Haszeldine, *ibid.*, 3416 (1956); (c) D. A. Barr, R. N. Haszeldine, and C. J. Willis, *ibid.*, 1351 (1961). Copolymers were also obtained.

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

[7] (a) D. A. Barr and R. N. Hazeldine, *J. Chem. Soc.*, 1151 (1960). (b) Previously, it had been reported that only nitrochlorofluoroalkanes were obtained from reaction of NOCl with fluoroölefins. R. N. Haszeldine, *ibid.*, 2075 (1953); Canadian Patent, No. 562,550 (1958).

[8] I. L. Knunyants and A. V. Fokin, *Bull. Acad. Sci. USSR*, **12**, 1462 (1957).

[9] The equilibration of nitrosyl fluoride with fluorocarbonyl compounds was described in a previous paper.[2]

[10] The only major competing side reaction under our conditions was the dimerization of tetrafluoroethylene to octafluorocyclobutane.

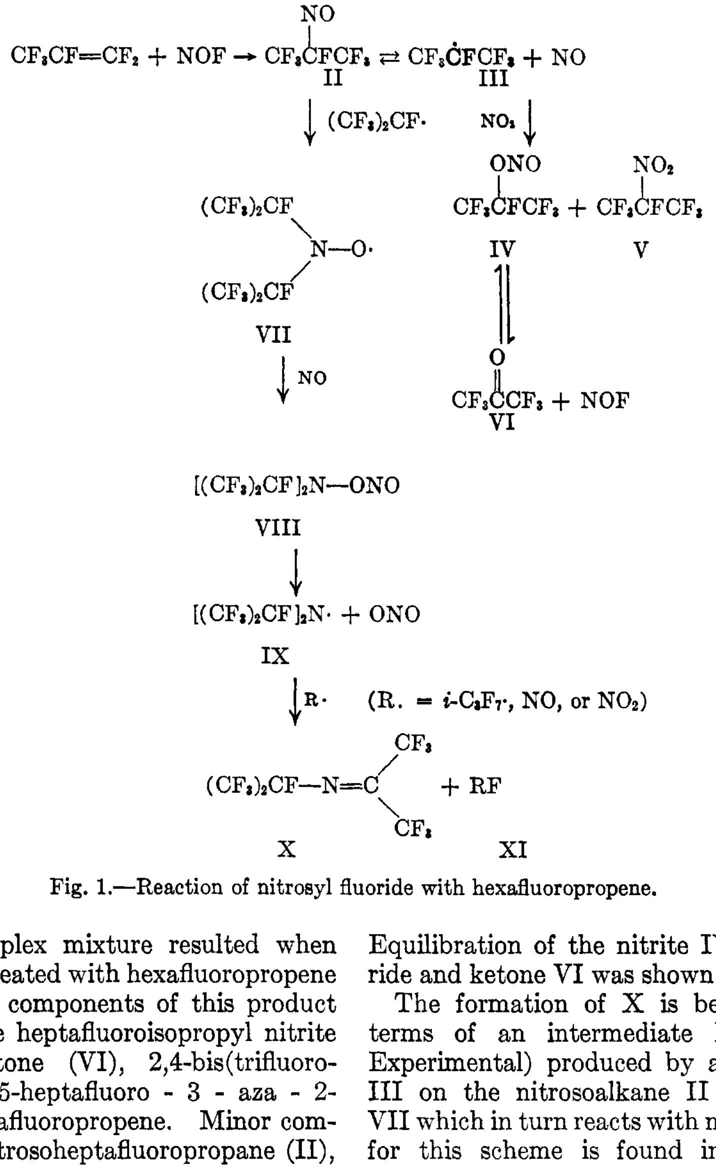


Fig. 1.—Reaction of nitrosyl fluoride with hexafluoropropene.

An extremely complex mixture resulted when nitrosyl fluoride was heated with hexafluoropropene at 120°. The major components of this product mixture (Fig. 1) were heptafluoroisopropyl nitrite (IV),[2] hexafluoroacetone (VI), 2,4-bis(trifluoromethyl) - 1,1,1,4,5,5,5-heptafluoro - 3 - aza - 2-pentene (X), and hexafluoropropene. Minor components included 2-nitrosoheptafluoropropane (II), 2-nitroheptafluoropropane (V), octafluoropropane (XI, R = C_3F_7), nitrosyl fluoride, and probably nitryl fluoride.

These results are rationalized as outlined in Fig. 1. In this scheme, further reaction of the intermediate nitroso compound II accounts for the complex array of products. Thermal homolytic cleavage of the C—N bond[11a] in II produces the radical III and nitric oxide. Reaction of III with nitrogen dioxide (produced later in the scheme) gives both the nitrite IV and the nitro compound V. Equilibration of the nitrite IV with nitrosyl fluoride and ketone VI was shown[2] to occur readily.[11b]

The formation of X is best accounted for in terms of an intermediate N-nitrite VIII (see Experimental) produced by attack of the radical III on the nitrosoalkane II to give the radical VII which in turn reacts with nitric oxide. Support for this scheme is found in the photochemical transformation of trifluoronitrosomethane (XII) to the N-nitrite XIII.[5c,12]

$$\underset{\text{XII}}{CF_3NO} \xrightarrow{h\nu} \underset{\text{XIII}}{(CF_3)_2N\text{—}ONO} \qquad (2)$$

Cleavage of the appropriate N—O bond in VIII[12b] leads to radical IX which can lose a fluorine atom to NO, NO_9, $C_3F_7\cdot$, etc. to give X and XI.[13]

Additional support for this scheme is provided by the following control experiments. When an equimolar mixture of pure II[14] and hexafluoropro-

---

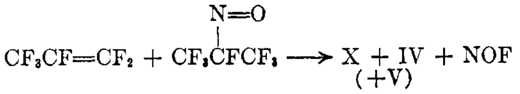
[11] (a) E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1954, p. 121. That the C—N bond is the weakest is consistent with the mass spectra of nitrosoperfluoroalkanes (see Experimental). Parent ions are weak or absent and *m/e* 30 is the most abundant ion in the spectrum of II. *Cf.* ref. 15b and 5c; (b) An additional equilibrium was probably established

$$(CF_3)_2CF\text{—}N{=}C(CF_3)_2 + NOF \rightleftarrows [(CF_3)_2CF]_2N\text{—}N{=}O$$

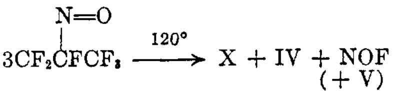
(*cf.* addition to $CF_3N{=}CF_2$, *vide infra*) but loss of nitrosyl fluoride during distillation would be facile (see Experimental).

[12] (a) R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 4172 (1955); (b) J. Jander and R. N. Haszeldine, *ibid.*, 696 (1954). The authors report that when XIII was heated at 100° (in a glass vessel), an unknown material (mol. wt. 183) having infrared absorption at 6.0 and 6.65 μ, was isolated. It is possible that the unknown material was a mixture of $(CF_3)_2NH$ (6.65 μ, mol. wt. 153) and $(CF_3)_2N\text{—}NO_2$ (6.0 μ, mol. wt. 198) arising from addition of hydrogen fluoride and nitryl fluoride, respectively, to $CF_3N{=}CF_2$, all predictable components on the basis of earlier considerations. The hydrogen fluoride could arise by reaction of nitryl fluoride with small amounts of moisture. More recently, the formation of trifluoronitromethane (38%) in this reaction was reported.[5c]

pene were heated in the absence of nitrosyl fluoride under the same conditions as in the above experiment, a product mixture similar to that shown in Fig. 1 was obtained, but consisting mainly of the



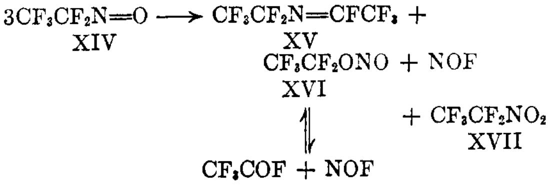
$$CF_3CF{=}CF_2 + CF_3\overset{\overset{N{=}O}{|}}{C}FCF_3 \longrightarrow X + \underset{(+V)}{IV} + NOF \qquad (3)$$



$$3CF_2\overset{\overset{N{=}O}{|}}{C}FCF_3 \xrightarrow{120^\circ} \underset{41\%}{X} + \underset{83\%}{IV} + \underset{(+\ V)}{NOF} \qquad (4)$$

azaalkene X, the nitrite IV, the starting olefin, and nitrosyl fluoride. Similarly, the same products were obtained when pure II was heated alone under the same conditions. The yields are based on the stoichiometry shown in (4).

Supplementary evidence for this scheme was obtained by heating pure pentafluoronitrosoethane (XIV)[15] under similar conditions. If the over-all mechanism in Fig. 1 is correct, the predicted main products are the azaalkene XV, the nitrite XVI, the nitroalkane XVII, and nitrosyl fluoride. These products were indeed produced[15] with significant amounts of XVII presumably arising from reaction of $CF_3CF_2\cdot$ on the nitrogen of nitrogen dioxide.



$$\underset{XIV}{3CF_3CF_2N{=}O} \longrightarrow \underset{XV}{CF_3CF_2N{=}CFCF_3} + \underset{XVI}{CF_3CF_2ONO} + NOF \qquad (5)$$
$$CF_3CF_2ONO \rightleftharpoons CF_3COF + NOF \qquad + \underset{XVII}{CF_3CF_2NO_2}$$

Due to the instability of the primary nitrite XVI,[2] it was obtained only in admixture with trifluoroacetyl fluoride and nitrosyl fluoride.[2]

Thus, pyrolysis of nitrosoperfluoroalkanes appears to be a general route to perfluoroazaalkenes.[16] For reasons discussed below, X is accessible directly from hexafluoropropene and nitrosyl fluoride.

Octafluoroisobutene and nitrosyl fluoride combine readily at low temperatures[1,6] to form *t*-nitrosononafluorobutane (XVIII). Apparently, im-

$$(CF_3)_2C{=}CF_2 + NOF \longrightarrow \underset{XVIII}{(CF_3)_3C{-}N{=}O} \qquad (6)$$

$$(CF_3)_3C{-}N{=}O \longrightarrow \underset{XVIIIA}{(CF_3)_3C{-}ONO} \qquad (7)$$

purities can catalyze the decomposition of XVIII. The formation of nonafluoro-*t*-butyl nitrite (XVIII-A) from a sample of XVIII containing some nitrogen dioxide occurred slowly at 25° in the absence of light suggesting facile cleavage of the C—N bond to give a relatively stable[16c] nonafluoro-*t*-butyl radical in accord with the mechanism outlined in Fig. 1.[16d]

Oxazetidine Formation.—Since oxazetidine formation from a nitrosoperfluoroalkane and a fluoroolefin may be studied independently, several factors governing the formation of oxazetidines from reaction of fluoroölefin with nitrosyl fluoride become apparent.

Synthesis of oxazetidines *via* this route (*e.g.* reaction 1) require higher temperatures for two reasons: (1) Formation of the intermediate nitroso compound from tetrafluoroethylene or hexafluoropropene does not occur at a significant rate at lower temperatures. (2) Higher temperatures favor predominant formation of oxazetidine as opposed to copolymerization[5] of the nitroso function with olefin.

Steric factors seem to play a dominant role in oxazetidine formation. Thus, in reaction 1 rapid formation of I competes successfully over other reactions of nitrosopentafluoroethane. In reaction 3 however, chain branching in the nitroso compound *and* the presence of a fluoroalkyl substituent on the olefin effectively serve to prevent formation of the corresponding oxazetidine so that other reactions of II become dominant. That chain branching in the nitroso compound alone does not prevent oxazetidine formation was shown by the following

---

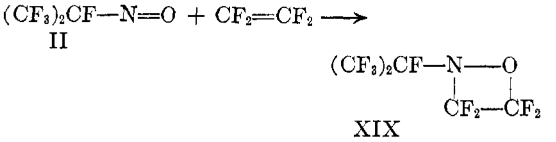
(13) The possibility that these transformations involve chain mechanisms has not been investigated. Formation of the radical VII is closely analogous to the formation of the stable *t*-butyl nitroxide radical which was reported recently: A. K. Hoffman and A. T. Henderson, *J. Am. Chem. Soc.*, **83**, 4671 (1961). The instability of VIII, if it is formed at all, and the probable intermediacy of VII are explicable in terms of the intrinsic stability of the three-electron N—O bond in VII as suggested by the above authors and by J. W. Linnett, *ibid.*, **83**, 2643 (1961).

(14) (a) Pure II was also synthesized by an alternative route: the ultraviolet irradiation of nitric oxide and heptafluoroisopropyl iodide[14b] in the presence of mercury; *cf.* ref. 5, 7b; (b) R. D. Chambers, W. K. R. Musgrave, and J. Savory, *Proc. Chem. Soc.*, 113 (1961); M. Hauptschein and M. Braid, *J. Am. Chem. Soc.*, **83**, 2383 (1961).

(15) (a) These same products were also isolated in small amounts in the synthesis of XIV (involving the irradiation of CF_3CF_2I and nitric oxide in the presence of mercury[14]), indicating that irradiation of XIV will effect the same transformations carried out, thermally, above; (b) *Cf.* also the recent report that $O_2NCF_2CF{=}NCF_2CF_2NO_2$ is formed when $O_2NCF_2CF_2NO$ is heated: V. A. Ginsburg, N. F. Privezentseva, V. A. Shpanskii, N. P. Rodionova, S. S. Dubov, A. M. Khokhlova, S. P. Makarov, and A. Ya. Yakubovich, *J. Gen. Chem. USSR*, **30**, 2391 (1960). In other investigations, the formation of azaalkenes from the thermal decomposition of nitrosofluoroalkanes was not reported. See, for example, ref. 5c, 12, and J. D. Park, A. P. Stefani, and J. R. Lacher, *J. Org. Chem.*, **26**, 4017 (1961).

(16) The only alternative known routes to perfluoroazaalkenes involve (a) pyrolysis of tertiary perfluoroamines to give mixtures [W. H. Pearlson and L. J. Hals, U. S. Patent 2,643,267 (1953)] and (b) pyrolysis of oxazetidines which are prepared from the nitrosoperfluoroalkanes.[5] See also, J. A. Young, T. C. Simmons, and F. W. Hoffman, *J. Am. Chem. Soc.*, **78**, 5637 (1956); K. A. Petrov and A. A. Neimysheva, *J. Gen. Chem. USSR*, **29**, 2662 (1960). (c) The stabilization of a radical by fluorine substitution has been previously described. M. Stacey, J. C. Tatlow, and A. G. Sharpe, "Advances in Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1960, p. 144; R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 3005 (1955). (d) It is interesting to note the possible steric effects shown by reactions of the various fluoroalkyl radicals with ONO to give either nitrites (reaction at oxygen) or nitro compounds (reaction at the sterically less favored nitrogen). The primary radical ($CF_3CF_2\cdot$) gives a mixture which is mainly the nitro compound. The secondary radical [$(CF_3)_2CF\cdot$] gives mainly the nitrite, while the *t*-butyl radical [$(CF_3)_3C\cdot$] apparently forms the nitrite exclusively. However, a reasonable interpretation based on electronic factors is also possible. *Cf.* similar results summarized for the ambident nitrite anion, D. J. Cram and G. S. Hammond, "Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1959, p. 215.

experiment in which XIX was formed[17a] although,

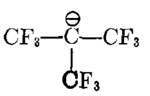


$$(CF_3)_2CF-N{=}O + CF_2{=}CF_2 \longrightarrow (CF_3)_2CF-N-O,\ CF_2-CF_2 \quad (8)$$

II XIX

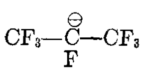
qualitatively, the reaction was slower than the corresponding reaction between nitrosopentafluoroethane and tetrafluoroethylene. Moreover, a trifluoromethyl substituent on the olefin will not prevent oxazetidine formation if a primary nitroso compound is used.[17b] As expected no oxazetidine was obtained from reaction of excess octafluoroisobutene with nitrosyl fluoride at 20°, although addition to form the *t*-nitrosobutane XVIII occurs readily at low temperatures (reaction 6).

Reactivity of Fluoroölefins.—Both the direction of addition of nitrosyl fluoride and the qualitative order of reactivity[18a] of fluoroölefins [$(CF_3)_2C{=}CF_2 > CF_3CF{=}CF_2 > CF_2{=}CF_2$] indicate that initial attack[18b] is by the anionic portion of the adding reagent (in this case, fluoride ion) to give a transition state with carbanion character. The direction of addition and the order of reactivity are both explicable in terms of greatest charge delocalization by "no-bond" resonance[19] in a carbanion with the largest number of β-fluorine atoms. Thus, the order of stability of the fluorocarbanions XX–XXII is tertiary > secondary > primary since



$CF_3-\overset{\ominus}{C}(CF_3)-CF_3$

XX



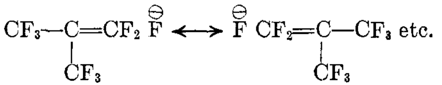
$CF_3-\overset{\ominus}{C}(F)-CF_3$

XXI

$CF_3\overset{\ominus}{C}F_2$

XXII

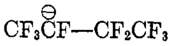
these ions can be stabilized by contributions from an additional nine, six, and three degenerate resonance extremes, respectively, of the type



$CF_3-\underset{CF_3}{C}{=}CF_2\ \overset{\ominus}{F} \longleftrightarrow \overset{\ominus}{F}\ CF_2{=}\underset{CF_3}{C}-CF_3$ etc.

XX

With internal olefins, steric factors possibly come into play since octafluoro-2-butene (68% *trans*, 32% *cis*) which would give an anion XXIII with five β-fluorine atoms for resonance stabilization, required a temperature of 250° indicating a lower

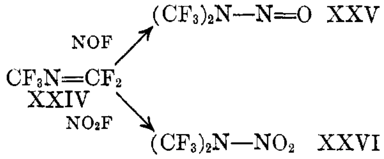


$CF_3\overset{\ominus}{C}F-CF_2CF_3$

XXIII

reactivity than tetrafluoroethylene. Since attack in this system must occur at a sterically less favorable secondary carbon atom, the 2-butene is much less reactive. An additional reason for the lack of reactivity of the butene is that 250° probably exceeded the critical temperature of both components, requiring either the incursion of a free radical process[18b] or the occurrence of an ionic addition in the vapor phase. The reaction took a somewhat different course, and the main products were pentafluoropropionyl fluoride, trifluoronitromethane and trifluoroacetyl fluoride. These products probably arose from oxidation of the intermediate nitrosobutane to the nitro compound followed by rearrangement to the nitrite. Decomposition of the resulting nonafluoro-2-butyl nitrite would be expected to lead to the above acid fluorides.[2,20]

Addition of Nitrosyl Fluoride and Nitryl Fluoride to Pentafluoroazapropene.—The addition of nitrosyl fluoride or nitryl fluoride to pentafluoroazapropene (XXIV) occurs rapidly and quantitatively at low temperatures to give N-nitroso-(XXV)[21] and N-nitrobis(trifluoromethyl)amine (XXVI),[22] respectively.



$CF_3N{=}CF_2$ (XXIV) $\xrightarrow{NOF}$ $(CF_3)_2N-N{=}O$ XXV

$CF_3N{=}CF_2$ (XXIV) $\xrightarrow{NO_2F}$ $(CF_3)_2N-NO_2$ XXVI

The ease of these additions is explicable in terms of the intermediate nitranion (XXVII) which can be stabilized by resonance involving six additional degenerate extremes as discussed above.

---

[17] (a) The yield of XIX was 45% and the other products appeared to be larger ring oxaazacycloalkanes. Although no oxazetidines could be found from reaction 3, small amounts of materials which appeared to be oxaazacyclohexanes were obtained; (b) The formation of oxazetidines from trifluoronitrosomethane and hexafluoropropene has been described.[6c]

[18] (a) The same direction of addition and order of reactivity was also observed for hydrogen halide additions to fluoroölefins. I. L. Knunyants, V. V. Shakina, and N. D. Kuleshova, *Izv. Akad. Nauk. SSSR Otd. Khim. Nauk*, **9**, 1693 (1960); (b) That the addition is an ionic process is supported by the following observations. The reaction between nitrosyl fluoride and tetrafluoroethylene was extremely slow below *ca.* 90° and 1000 p.s.i., conditions estimated to be near the critical constants of nitrosyl fluoride. There appeared to be a sudden increase in reaction rate (rapid pressure drop) when the pressure exceeded 1000 p.s.i. with the temperature still less than ~90°. Apparently, the addition occurred rapidly only in the highly polar condensed phase (liquified nitrosyl fluoride) containing dissolved coreactant (tetrafluoroethylene).

[19] J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Am. Chem. Soc.*, **72**, 408 (1950); J. D. Roberts, R. A. Clement, and J. J. Drysdale, *ibid.*, **73**, 2181 (1951).

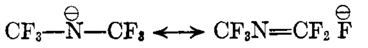
[20] Since considerable amounts of nickel fluorides were found in the reaction vessel from runs at 250°, decomposition of the nitrosyl fluoride to nitric oxide and nitrogen dioxide was likely and some of the products under these drastic conditions may be derived from reaction with nitrogen dioxide. However, the formation of CF_3CF_2COF probably could not arise from nitrogen dioxide reaction products since the addition of nitrogen dioxide to the butene would give products[8] of the type $CF_3\overset{NO_2}{C}F-\overset{ONO}{C}FCF_3$ which would decompose[2] to give 2-carbon fragments, or difunctional three-carbon compounds, such as the α-nitropropionyl fluoride.[2,8]

[21] J. A. Young, S. N. Tsoukalas, and R. D. Dresdner, *J. Am. Chem. Soc.*, **82**, 396 (1960). The vapor phase oxidation of XXIV is described;

$$2CF_3N{=}CF_2 + 1.5O_2 \longrightarrow (CF_3)_2NNO + 2COF_2\cdot$$

The authors postulate a sequence involving the formation and addition of nitrosyl fluoride to XXIV to explain the formation of XXV. The unidentified "fluffy white solid" found in their glass traps was most likely $(NO)_2SiF_6$ from reaction of nitrosyl fluoride with glass.[2]

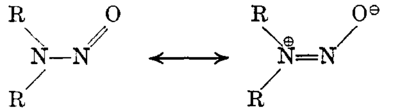
[22] J. A. Young, S. N. Tsoukalas, and R. D. Dresdner, *ibid.*, **80**, 3605 (1958).



$$CF_3\overset{\ominus}{N}CF_3 \longleftrightarrow CF_3N{=}CF_2\,\overset{\ominus}{F}$$

XXVII

Temperature Dependence of F^{19} N.m.r. Spectra.[23]—The proton n.m.r. spectrum at 25° of N,N-dimethylnitrosamine shows two equally intense peaks separated by a chemical shift of 26 c.p.s. at 40 Mc.[24] This result has been interpreted in terms of hindered internal rotation about the N—N bond of nitrosamines due to contributions of resonance extremes such as XXVIIIA (R = CH_3). A study of the temperature dependence of this spectrum has shown that the two peaks merge at 186° (when

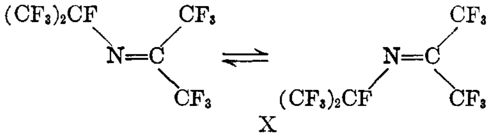


XXVIII XXVIIIA

the methyl groups become chemically equivalent) and the barrier to rotation was calculated to be 23 kcal./mole with a frequency factor of 0.7×10^{13} for this interconversion.[24]

The F^{19} n.m.r. spectrum of N,N-bis(trifluoromethyl)nitrosamine (XXVIII, R = CF_3), on the other hand, shows a single sharp resonance at 25° indicating equivalent CF_3 groups. Only when the temperature was lowered to *ca.* −110° did the resonance separate into two equally intense peaks *ca.* 135 c.p.s. apart at 56.4 Mc. corresponding to a mean lifetime (τ_A) of *ca.* 3.3×10^{-3} sec. for each rotamer at *ca.* −100° where the two peaks merge.[25] Preliminary estimates indicate a barrier of *ca.* 5 kcal./mole.[23] This pronounced lowering of the energy barrier for interconversion of rotamers of this molecule (when highly electronegative CF_3 groups are substituted for CH_3 groups) is explicable in terms of strong suppression of contributions from extreme XVIIIA when R = CF_3.

The temperature dependence of F^{19} n.m.r. spectra of both the oxazetidines and the azaalkenes described herein also illustrate greatly lowered barriers to inversion or rotation caused by the introduction of fluoroalkyl substituents. Thus, the F^{19} n.m.r. spectra of the azaalkene X as a function of temperature are shown in Fig. 2. The spectra at 58, 32, 5, and ∼ −10° represent temperatures[26b] at which peaks merge or splittings disappear. These spectra can be interpreted in terms of the following inversion process



X

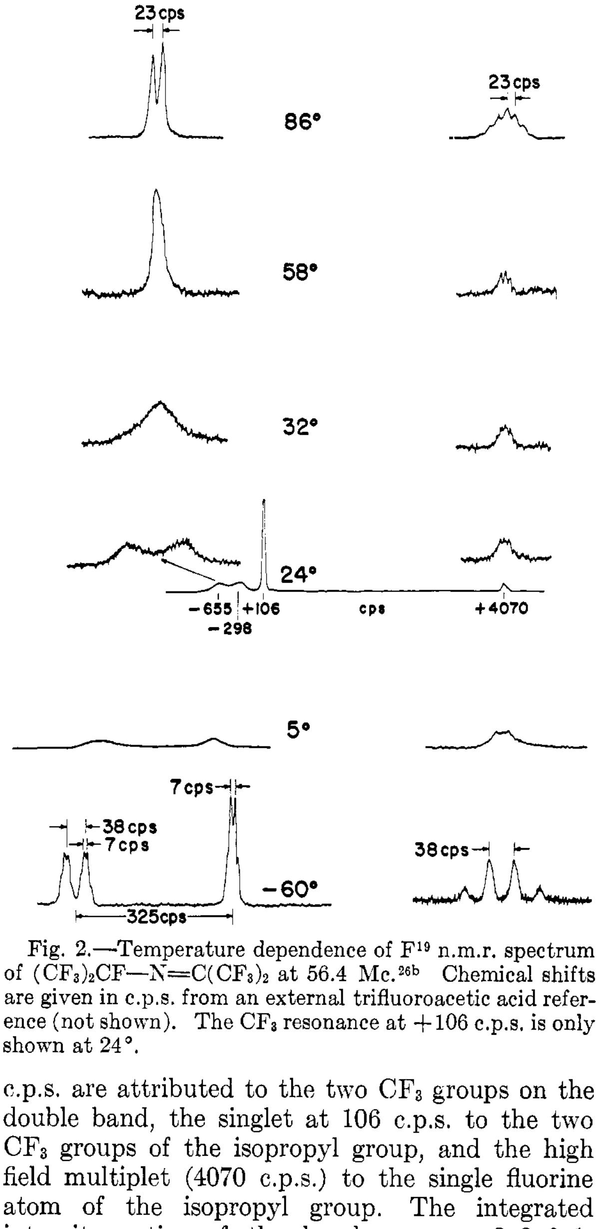
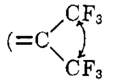


Fig. 2.—Temperature dependence of F^{19} n.m.r. spectrum of $(CF_3)_2CF—N{=}C(CF_3)_2$ at 56.4 Mc.[26b] Chemical shifts are given in c.p.s. from an external trifluoroacetic acid reference (not shown). The CF_3 resonance at +106 c.p.s. is only shown at 24°.

Thus, the two resonances at −655 and −298 c.p.s. are attributed to the two CF_3 groups on the double band, the singlet at 106 c.p.s. to the two CF_3 groups of the isopropyl group, and the high field multiplet (4070 c.p.s.) to the single fluorine atom of the isopropyl group. The integrated intensity ratios of the bands are *ca.* 3:3:6:1, respectively. Below 32°, the isomers resulting from inversion about nitrogen are "frozen out," and, at low temperatures, the long-range[26a] coupling between one of the $=C—CF_3$ groups and the high field isopropyl fluorine (*J* = 38 c.p.s.) is greater than the coupling between the two chemically shifted CF_3 groups



J = 7 c.p.s.).

At 32°, the two CF_3 peaks coalesce, and, at higher temperatures, when the rate of isomerization is rapid, the two equivalent CF_3 groups (on the double

---

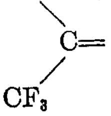
[23] Detailed n.m.r. studies of the systems described are in progress.

[24] C. E. Looney, W. D. Phillips, and E. L. Reilly, *J. Am. Chem. Soc.*, **79**, 6136 (1957).

[25] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

[26] (a) This coupling is between atoms separated by five bonds. Other examples of coupling of fluorine atoms through five bonds have been reported: A. Saika and H. S. Gutowsky, *J. Am. Chem. Soc.*, **78**, 4818 (1956); S. Andreades, *ibid.*, **84**, 864 (1962). "Through space" interactions are probably significant in these systems as well as in X.

bond) give rise to a doublet and split the isopropyl C—F into a septet ($J = 23$ c.p.s.). The isopropyl CF_3 groups give essentially a single resonance line (though somewhat broadened) at all temperatures examined.[26b] Since the mean lifetime in each state is a function of the inverse frequency separation of the peaks involved,[25] the merging of the chemically shifted CF_3 peaks (325-c.p.s. separation) occurs at a higher temperature[26b] than does the averaging of the various spin–spin splittings.

Mean lifetimes for each isomer were calculated at 32° where the CF_3 groups on the double bond become equivalent ($\tau_A = 1.4 \times 10^{-3}$ sec.); at 5°, where the doublet splitting for one  $\overset{\diagdown}{\underset{CF_3\diagup}{C}}{=}$ grouping and the C—F quadruplet splitting just disappear ($\tau_A = 1.2 \times 10^{-2}$ sec.) and at *ca.* −10°[26b] ($\tau_A = 6.4 \times 10^{-2}$ sec.) yielding an activation energy of *ca.* 13 ± 3 kcal./mole and a frequency factor of 10^{13} for the inversion process. These values may be compared to the barrier of *ca.* 25 kcal./mole for interconversion of nonfluorinated aldoxime isomers.[27] Whether this isomer interconversion involves inversion in the plane of the double bond or rotation about the double bond remains an interesting but unanswered question.[23]

The F^{19} n.m.r. spectrum of I as a function of temperature is typical of the behavior of fluorinated oxazetidines with respect to ring inversion about nitrogen. At 24°, the spectrum displays four peaks with integrated intensity ratios of 2:3:2:2 in the direction of increasing field. At low temperatures, each ring CF_2 splits into a four-line AB pattern due to "freezing out" of the pentafluoroethyl group on one side of the ring. The magnitude of the splitting for the CF_2N grouping is greater than that for the CF_2O fluorines.[23]

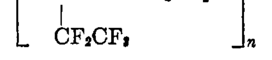
Experimental[28]

2-Pentafluoroethyl-3,3,4,4-tetrafluoro-1,2-oxazetidine (I).—To an evacuated 80-ml. shaker tube lined with prefluorinated Hastelloy "C" were added 5.9 g. (0.12 mole) of nitrosyl fluoride and 29.0 g. (0.29 mole) of tetrafluoroethylene. The reactor was closed and heated at 100° for 8 hr. while the autogenous pressure in the reactor dropped from 1170 to 260 p.s.i.g. Distillation of the recovered product gave 2.5 g., b.p. 19–22.5° (8%), and 14.0 g. (47%) of I. In other runs at higher pressures, yields of *ca.* 80% at 30% conversion were obtained.

Anal. Calcd. for C_4F_9NO: C, 19.29; F, 68.66; N, 5.63; mol. wt., 249.0: Found: C, 19.41; F, 68.75; N, 5.75; mol. wt., 249 (mass spec.).[28]

The infrared spectrum of I was blank in the 2000–1600-cm.$^{-1}$ region, showed strong C–F stretching centered at 1250 cm.$^{-1}$ and a sharp band at 1420 cm.$^{-1}$ which appears to be characteristic of this fluorinated ring system.[29] The infrared spectrum was identical to that of a sample of I prepared from nitrosopentafluoroethane and tetrafluoroethylene. The F^{19} n.m.r. spectrum of I was discussed above. The mass spectrum of I is summarized elsewhere.[28]

The only major side product, octafluorocyclobutane, was present in a lower boiling (−5 to 0°) fraction. Vapor phase chromatography[28] gave retention times of 1.7 min. and 3.9 min. for octafluorocyclobutane and I, respectively. Small amounts of copolymers of the type[5,7]



$$-\!\!\left[\!-\underset{\displaystyle CF_2CF_3}{\overset{}{N}}\!-\!O\!-\!CF_2CF_2\!-\right]_n\!\!-$$

were also obtained.

Reaction of Nitrosyl Fluoride with Hexafluoropropene.—As in the previous experiment, 12.7 g. (0.26 mole) of nitrosyl fluoride and 72 g. (0.48 mole) of hexafluoropropene were heated at 120° for 13 hr. with an autogenous pressure of 3000 p.s.i.g. The products boiled from −80° to 100°, but most of the material boiled in the ranges −34 to −30° (22.1 g.), 0–23° (10 g.), 23–37° (11.1 g.), and 42–56° (16.1 g.). All distillate fractions were resolved by vapor phase chromatography using the column and conditions described above[28] except for changes in column temperatures. The retention times for each compound are listed in Table I. Isolated peaks were identified by infrared and mass spectroscopy. In certain cases, compounds were isolated on a preparative v.p.c. scale for obtaining additional analytical or chemical data. The major components were hexafluoropropene, 17 g.; heptafluoroisopropyl nitrite[2] (IV, b.p. 29–30°) and hexafluoroacetone (VI), 11 g.; and 2,4-bis(trifluoromethyl)-1,1,1,4,5,5,5-heptafluoro-3-aza-2-pentene (X), 17 g. b.p. 52–53°.

TABLE I

VAPOR PHASE CHROMATOGRAPHY[a] OF PRODUCTS FROM REACTION OF NITROSYL FLUORIDE AND HEXAFLUOROPROPENE

Compound	Retention time, min.
CF_3COF	0.9[b]
$CF_3CF_2CF_3$	0.9
$CF_3N{=}CFCF_3$	1.1[b]
$CF_3CF{=}CF_2$	1.3
$(CF_3)_2C{=}O$	1.3
$(CF_3)_2CFNO$	1.5
$(CF_3)_2CFN{=}CFCF_3$	3.7[b]
$(CF_3)_2CFNO_2$	4.7
$(CF_3)_2CF{-}N{=}C(CF_3)_2$	5.7

[a] See ref. 28. [b] Only small amouts of these materials were present. Somewhat larger amounts were produced at higher reaction temperatures.

Anal. Calcd. for $C_6F_{13}N$: C, 21.64; F, 74.15; N, 4.21; mol. wt., 333.06. Found: C, 21.86; F, 74.16; N, 4.15; mol. wt., 333 (mass spec.).

The mass spectral pattern[28] of X is summarized in Table II, and the F^{19} n.m.r. spectrum was discussed above. X

---

[26] (b) The spectrum at *ca.* −10°, where the observable 7 c.p.s. quadruplet splitting between CF_3 groups disappears is not shown in Fig. 2. The fact that certain splittings were not discernible at 58° or below was probably a consequence of line broadening due to incomplete averaging of the widely separated CF_3 peaks up to this temperature.

(27) W. D. Phillips, private communication.

(28) (a) See ref. 41 in the previous paper.[2] N.m.r. band separations were determined using the conventional side band technique.[28b] Analytical vapor phase chromatography, unless otherwise specified, was carried out on a 6 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. Mass spectral data on all nitroso compounds, oxazetidines, and azaalkenes mentioned in this paper have been summarized and filed as Document No. 7299, with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C. (b) J. T. Arnold and M. G. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

(29) The *n*-heptafluoropropyl derivative and others[5c] absorb at 1418 cm.$^{-1}$.[5]

has an infrared absorption band at 1750 cm.$^{-1}$ (C=N stretching).

Table II

Mass Spectrum[a] of 2,4-Bis(trifluoromethyl)-1,1,1,4,5,5,5-heptafluoro-3-aza-2-pentene (X)

$(CF_3)_2C{=}NCF(CF_3)_2$

m/e	Relative abundance, %	Ion
333	0.2	$C_6F_{13}N^+$ (parent)
314	35.0	$C_6F_{12}N^+$
264	48.1	$C_5F_{10}N^+$
245	2.3	$C_5F_9N^+$
226	0.8	$C_5F_8N^+$
214	6.5	$C_4F_8N^+$
176	3.4	$C_4F_6N^{+b}$
169	13.1	$C_3F_7^+$
164	2.0	$C_3F_6N^+$
150	1.2	$C_3F_6^+$
126	1.0	$C_3F_4N^+$
119	8.7	$C_2F_5^{+b}$
114	0.8	$C_2F_4N^+$
100	3.4	$C_2F_4^+$
93	1.0	$C_3F_3^+$
76	5.2	$C_2F_2N^+$
69	100.0	CF_3^+
50	2.4	CF_2^+
31	9.5	CF^+

[a] See ref. 28. [b] Rearrangement ions.

Small samples of distillate which contained VI (b.p. −30°) or IV were treated with excess water to give an aqueous solution of hexafluoroacetone hydrate[2] in each case. The hydrate was converted to the hexafluoroacetone semicarbazone derivative.[29]

Minor components included the deep blue 2-nitrosoheptafluoropropane (II)[6] 4 g., b.p. −15 to −13°, 2-nitroheptafluoropropane (V), 4 g., b.p. 28–30°; octafluoropropane (XI. R = *i*-C_3F_7), 4 g., and small amounts of nitrosyl fluoride, trifluoroacetyl fluoride, carbonyl fluoride, 4-trifluoromethyl-1,1,2,4,5,5,5-octafluoro-3-aza-2-pentene [C=N stretching at 1800 cm.$^{-1}$, mol. wt. 283 (mass spec.)[28]], 1,1,1,3,4,4,4-heptafluoro-2-aza-2-butene [C=N stretching at 1790 cm.$^{-1}$, mol. wt., 183 (mass spec.)[28]], and a compound $C_9F_{19}NO$ (from mass spectral pattern, 2000–1600 cm.$^{-1}$ region blank in the infrared spectrum), which is believed to be an oxaazacyclohexane formed by reaction of 2 moles of hexafluoropropane with 1 mole of II.[30] An authentic sample of V was prepared by oxidation[5] of II,[6] which was independently prepared[14] from heptafluoroisopropyl iodide.[14b] The F^{19} n.m.r. spectrum (56.4 Mc.) of II showed a doublet at −44 and −37 c.p.s., and a septet centered at 5254 c.p.s. relative to trifluoroacetic acid (external reference) with relative integrated intensities in the ratio 7:1, respectively. Infrared and mass spectra[28] of all compounds except the azaalkenes were compared with spectra of the corresponding authentic samples.

Reaction of 2-Nitrosoheptafluoropropane (II) with Hexafluoropropene.—In an 80-ml. Hastelloy C shaker tube, 35.0 g. (0.175 mole of II and 39.0 g. (0.26 mole) of hexafluoropropene were heated at 120° for 13 hr. The recovered product (74 g.) was distilled giving fraction 1, b.p. −30° to −9°, 30 g.; fraction 2, b.p. −9 to −23°, 15 g.; fraction 3, b.p. 23–27°, 18 g.; fraction 4, b.p. 46–55°, 5 g.; fraction 5, b.p. 55–60°, 2 g.; and fraction 6, b.p. 60–70°, 2 g. Each fraction was analyzed by vapor phase chromatography as before and various peaks were collected for additional identification by infrared and mass spectroscopy. In general, a product distribution very similar to that obtained from the nitrosyl fluoride–hexafluoropropene reaction was found. Fraction 4 was mainly the azaalkene X (in 17% yield based on II), but contained some V and small amounts of X and 4-trifluoromethyl-1,1,1,2,4,5,5,5-octafluoro-3-aza-2-pentene. Fraction 1 was largely hexafluoropropene, *ca.* 5% VI, and *ca.* 3% II, while fraction 2 in addition to these three components contained 8% of V. Fraction 3 was mainly IV.

Pyrolysis of 2-Nitrosoheptafluoropropane (II).—In the same reactor used for the previous experiment, 20.0 g. (0.1 mole) of II was heated at 120° for 13 hr. under autogenous pressure. Approximately 1.3 g. of nitrosyl fluoride (probably contaminated with nitryl fluoride) was obtained, and a sample of the remaining gases contained VI, CF_3COF, CF_3NO_2, and COF_2. Distillation of the liquid products gave fraction 1, b.p. 26–28°, 6.5 g. (mainly IV, but contained some V), fraction 2, b.p. 29–40°, 3.0 g.; and fraction 3, b.p. 41–52° (mainly 46–52°), 4.5 g., which was shown by vapor phase chromatography and infrared spectroscopy to contain *ca.* 90% X. The spread in boiling point was probably due to the presence of either the N-nitrite VIII or the nitrosyl fluoride addition product[11b] which appeared to be decomposing during the distillation.

***t*-Nitrosononafluorobutane (XVIII).**—Into a dry, evacuated 300-ml. prefluorinated Monel vessel, cooled in liquid nitrogen, was distilled *in vacuo* 51.0 g. (0.255 mole) of octafluoroisobutene and 12.8 g. (0.26 mole) of nitrosyl fluoride. The vessel was closed and allowed to warm to room temperature. Distillation gave 57 g. (90%) of deep blue XVIII, b.p. 24–25°. The distillate solidified into a blue solid when cooled in ice water. When heated, XVIII reverted to starting materials, or to products from disproportionation, particularly in the presence of impurities. The sharp infrared N=O stretching absorption occurred at 1630 cm.$^{-1}$ and some absorption at 1720 cm.$^{-1}$ due to perfluoroisobutene could not be completely eliminated. The F^{19} n.m.r. spectrum (56.4 Mc.) showed only a single sharp resonance at −585 c.p.s. relative to trifluoroacetic acid as an external reference with a smooth decay pattern under rapid sweep conditions indicative of no splitting.

Anal. Calcd. for C_4F_9NO: F, 68.7; mol. wt., 249.0. Found: F, 70.2; mol. wt., 249 (deduced from mass spec.).[28]

Vapor phase chromatography of XVIII yielded a retention time of 8.1 min. on a 12-ft. column.[28] Unfortunately, perfluoroisobutene had the same retention time with the column and conditions used.

Nonafluoro-*t*-butyl Nitrite (XVIIIA).—Twenty-four grams of XVIII, contaminated with a small amount of nitrogen dioxide, was stored in a Monel cylinder for 2 months at room temperature. The bright yellow products were distilled giving fraction 1, b.p. 17–18°, 1.5 ml. (at −80°); fraction 2, b.p. 18–50°, 0.1 ml.; fraction 3, b.p. 50–55°, 7.2 g.; and fraction 4, b.p. 70–117° (with a considerable amount at 113–117°), 6.5 g. Fraction 3 (XVIIIA) was bright yellow, had very strong infrared absorption at 1830 cm.$^{-1}$ and displayed a single sharp F^{19} n.m.r. signal at +4025 c.p.s. (56.4 Mc.) relative to an internal fluorotrichloromethane reference (or *ca.* −397 c.p.s. (56.4 Mc.) from CF_3COOH). A sample was redistilled (b.p. 50–52°) and analyzed. Vapor phase chromatography showed that it was essentially one component.

Anal. Calcd. for $C_4F_9O_2N$: F, 64.5; N, 5.3. Found: F, 65.2; N, 4.9.

Pyrolysis of Nitrosopentafluoroethane (XIV).—Into an evacuated prefluorinated[28] 100-ml. reactor lined with Hastelloy "C" and cooled in liquid nitrogen was distilled *in vacuo* 11.0 g. (0.074 mole) of nitrosopentafluoroethane.[5] The reactor was heated at 100° for 6 hr. Since the mixture was still blue when transferred to a Pyrex flask, it was distilled back into the reactor and heated for an additional 6 hr. at 150°. The pale green product was distilled under dry nitrogen to give fraction 1, b.p. −13 to 0°, 1.5 g. and frac-

---

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

(30) Knunyants, *et al.*,[8] reported only two products (*i.e.*, II and IV) from the reaction of nitrosyl fluoride with hexafluoropropene at 150° in the presence of activated carbon. Yields were not given.

tion 2, b.p. 0–13°, 5.0 g. The products were colorless to yellow at 20° and pale green at −80°. The two fractions were resolved into their components by vapor phase chromatography. The various components were isolated and analyzed by infrared and mass spectroscopy. Fraction 1 contained *ca.* 36% nitrosyl fluoride, 14% CF_3COF (retention time 1.9 min.) along with some unstable XVI and 45% XVII (retention time 6.4 min.). Fraction 2 contained *ca.* 6% nitrosyl fluoride, 5% CF_3COF + XVI, 22% XV (retention time 6.0 min.), and 45% XVII. A peak at 93.5 min. (*ca.* 18% of fraction 2) was not identified. The infrared spectrum of XV showed C=N stretching absorption at 1790 cm.$^{-1}$ and a mol. wt. of 233 was deduced from the mass spectrum.[28]

The infrared and mass spectra of the other products were identical to spectra of authentic samples.

Isolation of Nonafluoro-3-aza-2-pentene (XV) during Synthesis of Pentafluoronitrosoethane (XIV).—To an evacuated 22.4-l. flask containing 5 lb. of mercury and equipped with an internal low-pressure mercury vapor lamp was added (at 25°) 66 g. (0.268 mole, 228 mm. partial pressure) of pentafluoroethyl iodide (Columbia Organic Chemicals Co.) and 232 mm. (0.3 mole) of nitric oxide. The mixture was shaken and irradiated for 8 hr. During this time, the pressure dropped from an initial 460 mm. to 253 mm. Helium was used to sweep the product through a column of mercury (to convert any nitrogen dioxide to nitric oxide) and a series of two traps cooled to −45° (freezing chlorobenzene bath) and finally into a third trap cooled in liquid nitrogen. The 45 g. of crude product which collected in the liquid nitrogen-cooled trap was distilled to give fraction 1, b.p. −43 to −42°, 13.5 g. (35%) of deep blue XVI[5] which was 96% pure by vapor phase chromatography[28] on a 12-ft. column[28] at 0° (retention time, 2.1 min.); fraction 2, b.p. −1 to −6°, 4.5 g.; and fraction 3, b.p. mainly 6–8°, 14.1 g. Fraction 3 was resolved by vapor phase chromatography[28] into 86% pentafluoroethyl iodide (retention time 6.0 min.), 4% XIV, 5% XVII, and 3% XV. Each peak was isolated and identified by infrared and mass spectroscopic comparison[28] with authentic materials. Fraction 2 consisted mainly of the latter two components. The F^{19} n.m.r. spectrum (56.4 Mc.) of XIV showed peaks at 378 (CF_3) and 2481 (CF_2) c.p.s. (CF_3COOH, external reference) with relative integrated intensities of 3:2, respectively.

Reaction of Nitrosyl Fluoride with Octafluoro-2-butene.—Little or no reaction between these compounds occurred below 200°.

In a 240-ml. reactor[28a] lined with Hastelloy "C" were combined 22 g. (0.45 mole) of nitrosyl fluoride and 95 g. (0.48 mole) of octafluoro-2-butene.[31] The closed vessel was heated at 200° for 12 hr. After removing the gaseous products, 12 g. of solid complex nickel fluorides was found in the reactor. Distillation of the gaseous products gave 14 g. boiling at −54° which was mainly CF_3COF and 61 g. boiling from −24 to 0° (mainly at 0°) which was a mixture of XVII and starting olefin. Experiments at 250° gave similar but more complex product mixtures. After vapor phase chromatographic separations, the products were identified as CF_3NO_2, CF_3COF, and CF_3CF_2COF. The presence of the unstable nitrites CF_3CF_2ONO and $CF_3CF_2CF_2ONO$ was indicated by infrared spectra and by the fact that these materials apparently decomposed during distillation liberating nitrosyl fluoride.[2] Infrared absorption of fractions believed to contain these materials appeared in the 1830-cm.$^{-1}$ region.

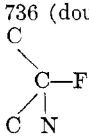
N-Nitrosobis(trifluoromethyl)amine (XXV).—Into an evacuated 300-ml. Monel[28] reactor cooled in liquid nitrogen was distilled *in vacuo* 12.0 g. (0.09 mole) of pentafluoro-2-azapropene,[5,16] and 4.5 g. (0.09 mole) of nitrosyl fluoride. The closed vessel was allowed to warm to 20°, and the product was distilled to give 16.0 g. (97%) of bright yellow XXV, the bulk of which boiled at −5 to −4°. The F^{19} n.m.r. spectrum (40.0 Mc.) showed a single peak at −650 c.p.s. relative to trifluoroacetic acid as an external reference or $\delta = -16.3$ p.p.m. (lit.[21] $\delta_{\text{ext}}^{\text{CF}_3\text{COOH}}$ −17.3 p.p.m., b.p. −4 to −3°).

Anal. Calcd. for $C_2F_6N_2O$: mol. wt., 182. Found: mol. wt., 172 (Victor Meyer).

The infrared spectrum contained all the bands tabulated previously.[21]

N-Nitrobis(trifluoromethyl)amine (XXVI).—In the same manner described in the previous experiment, reaction of 25.0 g. (0.188 mole) of pentafluoro-2-azapropene with 10.0 g. (0.154 mole) of nitryl fluoride gave 28.0 g. (92%) of pure XXVI, b.p. 20–21.5°. The F^{19} n.m.r. spectrum showed a single resonance at $\delta_{\text{ext}}^{\text{CF}_3\text{COOH}}$ −16.8 p.p.m. The infrared spectrum was in complete agreement with the infrared data reported previously[22] (lit.,[22] b.p. 17°).

Anal. Calcd. for $C_2F_6N_2O_2$: F, 57.58. Found: F, 57.44. The mass spectrum of XXVI is summarized elsewhere.[28]

2-Heptafluoroisopropyl-3,3,4,4-tetrafluoro-1,2-oxazetidine (XIX).—Into an evacuated 150-ml. Pyrex Carius tube cooled in liquid nitrogen were distilled *in vacuo* 11.0 g. (0.055 mole) of II and 6.0 g. (0.06 mole) of tetrafluoroethylene. The tube was sealed and heated at 100°. Since the mixture was still blue after 4 hr., heating was continued for a total of 20 hr. Some white solid [$(NO)_2SiF_6$] was found indicating the formation of nitrosyl fluoride which had attacked the glass.[2] Distillation of the product gave 3.4 g., b.p. 48–52°; and 1.4 g., b.p. 52–60°, of crude XIX in 45% yield. Higher boiling material, (*e.g.*, 2.6 g., b.p. 60–76°) probably included larger ring structures such as a perfluoroisopropyloxaazacyclohexane. Vapor phase chromatography[28] of the crude oxazetidine gave pure XIX with a retention time of 4.6 min. The infrared spectrum showed strong C—F absorption in the 1250-cm.$^{-1}$ region, was blank in the 1700-cm.$^{-1}$ region, and had a sharp peak[29] at 1420 cm.$^{-1}$. The F^{19} n.m.r. spectrum[23] (40.0 Mc.) at 20° displayed peaks at −67 [$(CF_3)_2$], +341 (CF_2O), 715, 736 (doublet, CF_2N), and 3309, 3330, 3351 c.p.s. (triplet  $\underset{\mathrm{C\ \ N}}{\overset{\mathrm{C}}{\mathrm{C{-}F}}}$) relative to trifluoroacetic acid (external reference) with integrated intensity ratios of 6:2:2 (doublet): 1 (triplet), respectively. The coupling constant (J = 21 c.p.s.) between the isopropyl fluorine and the two ring fluorine atoms was confirmed by the constancy of the splittings with varying oscillator frequency.

Anal. Calcd. for $C_5F_{11}NO$: mol. wt., 299.0. Found: mol. wt., 299 (mass spec.).[28]

---

(31) This material, purchased from Halocarbon Products Corp., Hackensack, N. J., was a mixture of *cis* and *trans* isomers.