

864. *Perfluoroalkyl Compounds of Nitrogen. Part V.¹ The Dimer (N-Nitritoamine) of Trifluoronitrosomethane.*

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The nuclear magnetic resonance, ultraviolet ($n_{\text{N}}-\pi^*$), and infrared spectra show that the dimer of trifluoronitrosomethane has the *N*-nitritoamine structure $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{NO}$ with free rotation about the $\text{C}_2\text{N}-\text{ON}$ and possibly the $\text{C}_2\text{NO}-\text{N}$ bond. The infrared spectra in the sodium chloride region have been assigned for $(\text{CF}_3)_2\text{NX}$ compounds with $\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{NO}, \text{NO}_2, \text{O}\cdot\text{NO}$, and $\text{N}(\text{CF}_3)_2$.

The dimer is formed slowly when the gaseous monomer is left in the dark, and faster when it is exposed to red light. It decomposes slowly in the dark, faster in the light, to give fluoropicrin, some pentafluoro-2-azapropene, traces of the *N*-nitroamine $(\text{CF}_3)_2\text{N}\cdot\text{NO}_2$, and fragmentation products.

TRIFLUORONITROSOMETHANE² photodimerises³ irreversibly on the absorption of red light to give the pale orange *N*-nitritoamine $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{NO}$. As described in Part VI,³ the dimer is formed quantitatively and readily separated only if visible and ultraviolet light of shorter wavelength (which decomposes monomer and dimer) is excluded, and reactions times are short, with incomplete conversion, since the dimer is unstable at room temperature.

The ¹⁹F nuclear magnetic resonance spectrum (for which we thank Dr. R. E. Richards and his co-workers) of the dimer consists of a single sharp fluorine resonance, as for $(\text{CF}_3)_2\text{NX}$ compounds such as the nitrosoamine,^{4a} the mercurial^{4b} $\text{Hg}[\text{N}(\text{CF}_3)_2]_2$, the acid chloride⁵ $(\text{CF}_3)_2\text{N}\cdot\text{COCl}$, and the hydrazine derivative⁶ $(\text{CF}_3)_2\text{N}\cdot\text{N}(\text{CF}_3)_2$. This is taken to mean that the fluorine atoms are all equivalent, for although spin-spin coupling between non-equivalent α -fluorine atoms in saturated compounds is often very slight, it is strong between β - or γ -fluorine, and the CF_3 resonance is readily resolved into its components in amines such as $(\text{C}_2\text{F}_5)_2\text{N}\cdot\text{CF}_3$ ⁷ or the piperidine derivative $\text{C}_5\text{F}_{10}\text{N}\cdot\text{CF}_3$.⁸ The simple spectrum of the dimer suggests that rotational isomerism, as shown by alkyl nitrites⁹ and dialkyl-*N*-nitrosoamines,¹⁰ is absent at room temperature for the perfluorinated *N*-nitritoamine, as for the corresponding nitrosoamine;^{4a} the fluorine substituents reduce the availability of the amino- n_{N} -electrons, and therefore the $(\text{CF}_3)_2\text{N}-\text{X}$ bond order, allowing free rotation.

Electronic Absorption.—The dimer absorption¹ in the near ultraviolet region, with $\epsilon_{\text{max.}}$ 19.7 at 3720 Å, $\epsilon_{\text{min.}}$ 9.6 at 3230 Å for the gas, has the intensity and energy of an $n_{\text{N}}-\pi^*$ band. There is a slight red shift with hydrocarbon solvents, and the expected blue shift with polar solvents,¹ in which solvolysis can occur, *e.g.*, the spectrum of ethyl nitrite appears when the dimer is dissolved in ethanol.

The colour of the dimer is due to the tail in the visible part of the near-ultraviolet band, and to one of the decomposition products, nitrogen dioxide. When this is removed the absorption is structureless,¹ in contrast to the banded absorption, due to the $\text{N}:\text{O}$ stretching vibration in the excited state, of alkyl nitrites and nitrosoamines. The continuum corresponds to dissociation of the dimer, as expected for a labile molecule, with 77 kcal. mole⁻¹ available at 3720 Å.

¹ Part IV, *J.*, 1957, 3904.

² Mason (née Banus), Part I, *J.*, 1953, 3755.

³ Mason (née Banus), following paper.

⁴ Young, Tsoukalas, and Dresdner, *J. Amer. Chem. Soc.*, (a) 1960, **82**, 396; (b) 1958, **80**, 3604.

⁵ Young and Dresdner, *J. Org. Chem.*, 1958, **23**, 1576.

⁶ Young, Durrell, and Dresdner, *J. Amer. Chem. Soc.*, 1959, **81**, 1587.

⁷ Petrakis and Sederholm, *J. Chem. Phys.*, 1961, **35**, 1243.

⁸ Müller, Lauterbur, and Svatos, *J. Amer. Chem. Soc.*, 1957, **79**, 1807.

⁹ Tarte, *J. Chem. Phys.*, 1952, **20**, 1570.

¹⁰ Looney, Phillips, and Reilly, *J. Amer. Chem. Soc.*, 1957, **79**, 6136.

The nitroso- $n_{\text{O}}-\pi^*$ absorption of the dimer (at 2695 Å with ϵ_{max} 1.8 for the monomer¹⁾ is probably concealed by the strong $\pi-\pi^*$ absorption (cf. alkyl nitrites and nitrosoamines), which begins at 3100 Å and reaches $\epsilon \sim 1000$ at 2100 Å.

The $n_{\text{N}}-\pi^*$ absorption limits formulations of the dimer to the *N*-nitritoamine (since the empirical formula is given by quantitative synthesis and analysis, and the molecular weight by gas density, and the two CF_3 groups are equivalent). It is inconsistent with structures containing N-O-tetracycles (since they lack π -orbitals), or azo-ether groups (which absorb beyond the azo-group $n_{\text{N}}-\pi^*$ absorption, at 3570, 2640 Å for $\text{CF}_3\cdot\text{N}=\text{N}\cdot\text{CF}_3$ ¹¹⁾, or with the dimeric alkylnitroso-structure (which lacks n_{N} electrons and shows only intense $\pi-\pi^*$ absorption¹²⁾. The isomeric *N*-nitroamine has different properties,⁴ and its ultraviolet absorption probably resembles that of the parent compound $\text{Me}_2\text{N}\cdot\text{NO}_2$, which has ϵ_{max} 6300 at 2400 Å in dioxan solution,¹³ and 8000 at 2380 Å in water.¹⁴

The ultraviolet as well as the nuclear magnetic resonance spectrum suggests that the N·O·N·O system is non-conjugated. A blue shift would be expected on electronegativity

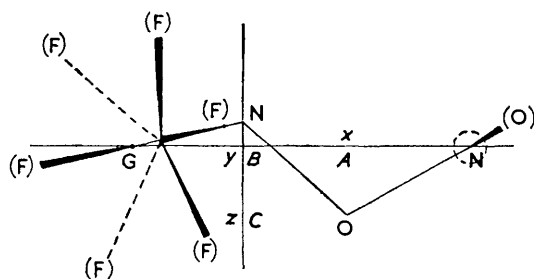


FIG. 1. *trans*-Skew $(\text{CF}_3)_2\text{N}\cdot\text{O}\cdot\text{NO}$ Projection on GNON plane, where G is the centre of gravity of the two CF_3 groups.

grounds for an *N*-nitrite in relation to a *C*-nitrite, with a further blue shift for the extended delocalisation (cf. $\text{Me}_2\text{N}\cdot\text{NO}$ with ϵ_{max} 100 at 3630 Å, MeNO ¹⁵ with λ_{max} at 6800 Å), since for planar N·O·N·O three of the π -orbitals would be filled, raising the lowest unoccupied π^* -orbital above the level for a *C*-nitrite: yet these absorb at shorter wavelengths than the dimer [$\text{MeO}\cdot\text{NO}$ has ϵ_{max} 89 at 3390 Å, and $(\text{CF}_3)_2\text{CF}\cdot\text{O}\cdot\text{NO}$ ¹⁶ has ϵ_{max} 60 at 3480 Å]. The delocalisation, with two of the filled π -orbitals partly anti-bonding, does not warrant the promotion of the n -electrons, which in addition are stabilised by the CF_3 groups. These (in contrast to alkyl groups) repel the n_{N} and n_{O} electrons, which repel each other. The nuclear magnetic resonance, ultraviolet, and (below) the infrared spectra support the expectation that the amino-nitrogen in the dimer is pyramidal, and suggest the possibility of free rotation about the N·O·N·O as well as about the N·O·N·O bond. The relatively high barrier in the alkyl nitrites,¹⁷ 8–10 kcal. mole⁻¹, argues against this, but heptafluoroisopropyl nitrite also shows no rotational isomerism at 20°, on the nuclear magnetic resonance.¹⁶

Infrared Absorption.—The infrared spectrum of the dimer is readily assigned to the nitritoamine structure, by comparison with the spectra of some oxides of nitrogen, including the frozen metastable molecules O·N·O·N·O and O·N·O·NO₂,¹⁸ and of the compounds $(\text{CF}_3)_2\text{NX}$ where X is H, F, NO, Cl, NO₂, Br, or $\text{N}(\text{CF}_3)_2$, in the sodium chloride region.

¹¹ Dacey and Young, *J. Chem. Phys.*, 1955, **23**, 1302.

¹² Gowenlock and Trotman, *J.*, 1956, 1670.

¹³ Jones and Thorn, *Canad. J. Res.*, 1949, **27**, B, 828.

¹⁴ Kortüm and Finckh, *Z. phys. Chem.*, 1940, B, **43**, 32.

¹⁵ Tarte, *Bull. Soc. chim. belges*, 1954, **63**, 525.

¹⁶ Andreades, *J. Org. Chem.*, in the press.

¹⁷ Gray and Reeves, *J. Chem. Phys.*, 1960, **32**, 1878; Piette and Anderson, *ibid.*, 1959, **30**, 899.

¹⁸ Fateley, Bent, and Crawford, *J. Chem. Phys.*, 1959, **31**, 204; Hisatsune, Devlin, and Wada, *ibid.*, 1960, **33**, 714.

To help the assignment to symmetry species, the band contours and *PR* separations were compared with those calculated for the symmetric¹⁹ or asymmetric²⁰ tops to which the molecules approximate. $(CF_3)_2NX$ molecules belong effectively to the point group C_s if X lies in the plane bisecting the CNC angle. This is true for monatomic X, and was assumed for X = NO and NO₂, and also for X = O·NO since in the *trans*-skew conformation (Fig. 1) in which the *n*-electron repulsions may be least, only the nitroso-oxygen atom is out of the plane. The $(CF_3)_2N·N(CF_3)_2$ molecule has C_2 symmetry if the set C¹N¹N²C⁴ is assumed planar and C¹N¹C² turned through 70° about the N-N bond relative to C³N²C⁴. Moments of inertia calculated with assumed axes were checked by a method²¹ requiring no choice of axes. The amine and fluoroamine are prolate, and the nitritoamine oblate, (accidental) near-symmetric tops, and the other molecules are asymmetric.

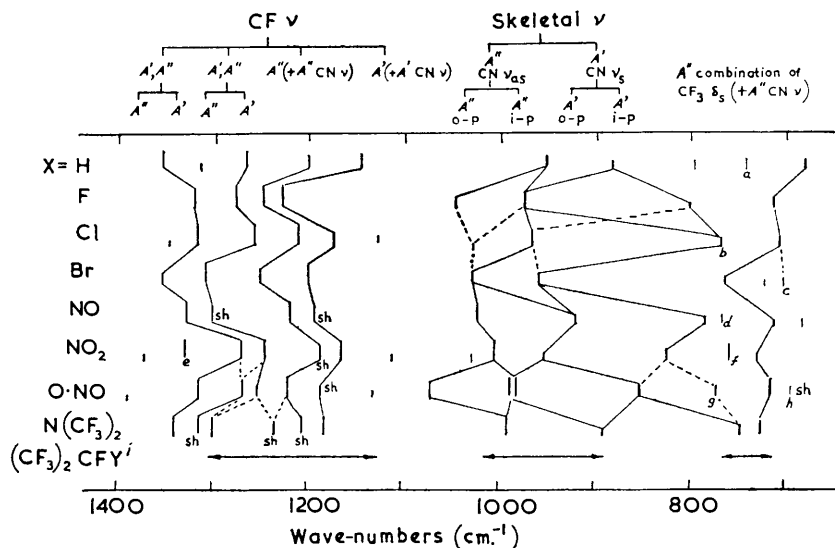


FIG. 2. Correlation diagram of $(CF_3)_2NX$ fundamental frequencies, with approximate description of the vibrations. Broken lines show alternatives. sh means shoulder, o-p out-of-phase, i-p in-phase. *a*, NH $A''\delta$. *b*, or NCl ν . *c*, or A' combination of $CF_3 \delta_s$, or etc. *d*, NNO $A' \delta$. *e*, NO₂ ν_s . *f*, NO₂ $A' \delta_s$. *g*, ?ONO δ . *h*, ?NON δ . *i*, Chambers, Musgrave, and Savory, *J.*, 1962, 1993.

Some of the band envelopes were of recognizable type for $(CF_3)_2NX$ compounds with X mono- or di-atomic, notably at lower frequencies where the resolving power of the spectrophotometer is better, but they are less distinctive for the nitroamine and nitritoamine. For the hydrazine they were not very discriminative because the *A*, *B*, and *C* *PR* separations are very similar. An assignment that leans on contour types is that of the A'' (out-of-plane) combination of the CF_3 symmetric deformation (δ_s) modes.


As the correlation diagram shows (Fig. 2), the bands fall into about five groups derived roughly from the double-bond stretching, the CF stretching, the skeletal stretching (C, N, O, and NF), the CF bending (perfluoroisopropyl compounds show the three last-named groups), and NX vibrations. All bands stronger than "very weak," and their contour types, have been reasonably accounted for.

Double-bond region. The Table shows that the N:O stretching (ν) vibration of the dimer

¹⁹ Gerhard and Dennison, *Phys. Rev.*, 1933, **43**, 197.
²⁰ Badger and Zumwalt, *J. Chem. Phys.*, 1938, **6**, 711.
²¹ Hirschfelder, *J. Chem. Phys.*, 1940, **8**, 431.

at 1803, 1830 cm^{-1} resembles that of compounds with the nitroso-group attached to NO or ON or halogen, but is at some 200 cm^{-1} higher frequency than for nitroso-compounds, *N*-nitrosoamines, or alkyl nitrites (unless the alkyl group is fluorinated). The order of frequencies roughly reflects the electronegativities of the attached groups (the mass effects do not vary widely), as well as the bond order in the nitroso-group, which may then be higher in the dimer than in an unsubstituted alkyl nitrite. In this case, combinations such as (1068 + 770) or (980 + 850) may perhaps explain the splitting of the N:O ν frequency.

N:O stretching modes in the dimer and related compounds (cm^{-1}).

| High | | Low | |
|---|---|--|------------|
| NO | 1876 | MeO·NO ⁸ <i>cis</i> | 1625 |
| NOF, Cl, Br, resp. | 1844, 1800, 1801 | <i>trans</i> | 1681 |
| (NO) ₂ * sym. <i>cis</i> | 1864 | (CF ₃) ₂ N·NO ^{4a} | 1644 |
| asym. <i>cis</i> | 1773 | Me ₂ N·NO | 1489 |
| asym. <i>trans</i> . | 1740 | CF ₃ ·NO ²⁵ | 1595 |
| ON·O·NO* | 1830, 1843, 1905 | Me ₃ C·NO | 1574 |
| O ₂ N·NO | 1863,* 1830 | HNO, DNO, ‡ resp. | 1570, 1560 |
| O ₂ N·O·NO* | 1829 | | |
| (CF ₃) ₂ N·O·NO | 1803, 1830 | | |
| (CF ₃) ₂ CF·O·NO ¹⁶ | 1840 | | |
|  | 1860 (strong), 1750 (v. weak), perhaps <i>trans</i> and <i>cis</i> , respectively | | |
| R·N(NO)·O·NO † | 1820, 1730, 1665 | | |

The compounds are gaseous unless otherwise described.

* Unannealed solid or solid solution at low temperatures, including metastable compounds. Different values may apply to different matrices (CO₂, argon, etc.).¹⁸ † Cyclohexane solution; the compound is discussed in Part VI.⁹ Cf. Donaruma and Carmody (*J. Org. Chem.*, 1957, **22**, 635). ‡ Brown and Pimentel, *J. Chem. Phys.*, 1958, **29**, 883.

The only other strong bands in this region are due to the *A'* (in-plane) δ mode in the amine at 1508 cm^{-1} (cf. 1500—1550 for secondary amides,²² 1518 for Me·NH·OH and 1600 cm^{-1} for Me·NH·OMe²³), the N:O ν mode in the nitrosamine at 1644 cm^{-1} (150 cm^{-1} higher than for Me₂N·NO¹⁰), and the NO₂ antisymmetric stretching (ν_{as}) mode for the nitroamine at 1670 cm^{-1} (about 100 cm^{-1} higher than for Me₂N·NO₂²⁴).

CF stretching modes, 1100—1350 cm^{-1} . An "isolated" CF₃ group as in CF₃H gives two strong bands in the 1100—1200 cm^{-1} region, one for the ν_{s} and the other for the two degenerate ν_{as} CF₃ modes. In CF₃·NO²⁵ the *A'* and *A''* CF₃ ν_{as} modes are split, presumably by coupling with, respectively, the NO bending and the NO torsional mode, and the ν_{s} frequency is pushed up to nearly 1300 cm^{-1} by the CN ν mode. In (CF₃)₂NX molecules, each of these three CF₃ ν vibrations gives an in-plane and an out-of-phase combination for the two groups. The combinations of the CF₃ ν_{s} modes will be split by coupling with the *A'* and *A''* CNC ν modes, but those of the ν_{as} modes, with transition moment orthogonal to the CN bond direction, may well remain degenerate while the molecule has C₂ symmetry.

Thus we find four very strong bands in the region 1140—1360 cm^{-1} for (CF₃)₂NX compounds with X = H, F, NO, Cl, or Br, and five for X = NO₂ of which one is the NO₂ ν_{s} frequency (at 1305 cm^{-1} for Me₂N·NO₂²⁴). The dimer gives five very strong bands and the hydrazine six, which suggest that the staggered conformations allow further coupling of the CF ν with skeletal modes, removing, successively, the two remaining degeneracies. This description of the vibrations is a rough one, the non-totally symmetric stretching modes having a substantial bending component, since carbon and fluorine atoms are

²² Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958.

²³ Davis and Spiers, *J.*, 1959, 3971.

²⁴ Jonathan, *J. Mol. Spectroscopy*, 1960, **5**, 101.

²⁵ Mason (née Banus) and Dunderdale, Part II, *J.*, 1956, 754.

similar in mass. There are some very weak bands which may perhaps arise from components of the supposed degenerate combinations by interaction with other modes, but these cannot be distinguished readily from overtones or combination bands in this region.

Skeletal stretching frequencies, 750—1050 cm.⁻¹. The (CF₃)₂NX vibrations in this region, when the atom X is much lighter (H) or heavier (Cl, Br) than nitrogen, are the A'' and A' CNC ν modes (1073 and 931 cm.⁻¹ for Me₂NH); the contours of the (CF₃)₂NH bands in particular are characteristic of the appropriate species.

In the remaining compounds the CNC ν vibrations also couple with those of NF, NN, and N·O. Thus there are three bands in this region for (CF₃)₂NF, corresponding in order of decreasing frequency largely to the A'', the antisymmetric A', and the A' breathing modes of C₂NF (or else the intermediate frequency may be that of a second CNC ν_{as} mode, the band contours being less helpful here); and similarly for the C₂NN modes in the nitrosoamine (cf. 1016, 848, and 795 cm.⁻¹ for Me₂N·NO¹⁰) and the nitroamine.

In the nitritoamine spectrum, the four bands at 1068, 980—985, 850, and 770 cm.⁻¹ may represent approximately the out-of-phase and in-phase (CNC ν_{as} + NON ν_{as}) combinations, and the out-of-phase and in-phase (CNC ν_s + NON ν_s) combinations, respectively; cf. 1060, 1005, 940, and 775 cm.⁻¹ for the Me₂N·OMe skeleton.²³ The oxides ON·O·NO, ON·O·NO₂, and O₂N·O·NO₂,¹⁸ and *cis*- and *trans*-MeO·NO,⁹ all have N·O ν frequencies between 800 and 970 cm.⁻¹. The (CF₃)₂N·N(CF₃)₂ skeletal stretching system seems to cover a larger frequency range. Weaker bands in this region may be overtones of strong bands due to the bending of bonds to fluorine.

CF bending frequencies, 680—780 cm.⁻¹. The CF₃ δ_s frequency for CF₃X compounds, where X is H, Cl, Br, I, NO, NO₂, or NF₂, etc., is in the range 700—780 cm.⁻¹ (some 200 cm.⁻¹ higher than for the δ_{as} mode). Suitable bands in the (CF₃)₂NX spectra are as follows (cm.⁻¹): when X is H 680, F 712, Cl 706, Br 762 (?720, ?699), NO 715, ONO 715, NO₂ 729, and N(CF₃)₂ 723. The contours of these bands for X = H, F, Cl, NO, and NO₂ point clearly to an A'' vibration, the remainder being equivocal. They are therefore assigned to the out-of phase combination of the two CF₃ δ_s modes, coupled with the A'' ν CN mode, to split the in- and the out-of-phase combinations; the former (coupled with the A' CN ν) is then at lower frequencies.

NX frequencies, 600—800 cm.⁻¹. For X = H a rather broad weak band at 739 cm.⁻¹ may arise from the A' NH δ mode (~700 cm.⁻¹ for hydrogen-bonded proteins and secondary amides,²² 828 cm.⁻¹ for Me·NH·OH and 803 for Me·NH·OMe²³). For X = Cl a weak band at 768 cm.⁻¹ with an A'-type contour could represent the NCl ν vibration (cf. 760—800 cm.⁻¹ for cyanuric acids²⁶), if we place the CNC ν_{as} and ν_s modes at 1027 and 965 cm.⁻¹, but in view of the low intensity of the former and the A''-type contour of the latter, it is more likely that the NCl ν vibration has a lower frequency (cf. 595 cm.⁻¹ for NOCl).

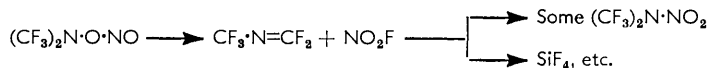
In the 550—800 cm.⁻¹ region are the scissor δ frequencies of -O·NO, -NO₂, and >N·NO groups, whether attached to carbon, oxygen, or nitrogen, *e.g.*, (cm.⁻¹) 617 and 565 for *cis*- and *trans*-MeO·NO,⁹ 699 for ON·O·NO,¹⁸ 612 for Me₂N·NO₂,²⁴ 682 for liquid (associated) Me₂N·NO, below 660 for the gas. Bands which are perhaps explicable in this way are at 765 cm.⁻¹ for the nitrosoamine and 758 cm.⁻¹ for the nitroamine, the contours indicating A' vibrations. A pronounced shoulder at 692 cm.⁻¹ (with one at 1390 cm.⁻¹ as its overtone) in the nitritoamine spectrum may arise from the O·NO δ mode, or this may have a lower frequency.

Preparation and Storage.—The dimer is a pale orange gas when pure (cooling to a straw-coloured liquid or cream-coloured solid), but it soon darkens to red-brown with the production of nitrogen dioxide. It is formed and slowly decomposes when trifluoronitrosomethane gas is stored in the dark, and its rate of formation is increased in diffuse daylight or on irradiation. However, it is difficult to separate pure dimer by distillation from the mixture including decomposition products, and it is best prepared by short, intense

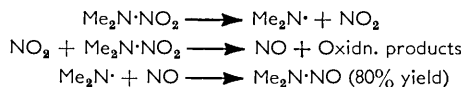
²⁶ Peterson, Grzeskowich, and Jules, *J. Org. Chem.*, 1960, **25**, 1595.

irradiation (with incomplete conversion), preferably with the red light that the nitroso-compound absorbs, and without the light below 5000 Å that the dimer absorbs.

When kept as a gas or liquid in the dark, or faster in the light, the dimer decomposes to form a mixture containing nitrogen, nitrous oxide, nitrogen dioxide, carbon dioxide, silicon fluoride, and fluorocarbon derivatives as found in the decomposition of trifluoronitrosomethane (which proceeds, at least in part, through the dimer, as described in Part VI³⁾; fluoropicrin, pentafluoro-2-azapropene, and a little of the *N*-nitroamine, perhaps formed by the reaction



This nitroamine⁴ is more stable than its unfluorinated analogue. $(\text{CF}_3)_2\text{NX}$ compounds which lose a fluoride XF on pyrolysis to form the azapropene in a reversible reaction, include the amine $(\text{CF}_3)_2\text{NH}$,^{4b,27} the mercurial $[(\text{CF}_3)_2\text{N}]_2\text{Hg}$,^{4b,6} and the nitrosoamine $(\text{CF}_3)_2\text{N}\cdot\text{NO}$,^{4a} all of which have been prepared by the addition of the fluoride XF to the azapropene, and the acid fluoride $(\text{CF}_3)_2\text{N}\cdot\text{COF}$ (for which the reverse reaction was not described^{5,28}). The corresponding aza-alkenes are formed from nitroso-compounds $\text{R}_\text{F}\cdot\text{NO}$, where R_F is C_2F_5 or iso- C_3F_7 ,¹⁶ or $\text{CF}_2\text{Cl}\cdot\text{CF}_2$ or $\text{CF}_2\cdot\text{NO}_2\cdot\text{CF}_2$,²⁹ either through the nitritoamine $(\text{R}_\text{F})_2\text{N}\cdot\text{O}\cdot\text{NO}$ or from the radical $(\text{R}_\text{F})_2\text{N}\cdot\text{O}\cdot$ formed by the addition of an R_F radical to the nitroso-compound; mechanisms are discussed in the following paper. The elimination from the nitritoamine might be intramolecular or might involve the $(\text{R}_\text{F})_2\text{N}\cdot$ radical, as *e.g.*, in the pyrolysis of dimethylnitroamine.³⁰



EXPERIMENTAL

Ultraviolet and visible spectra were measured with gaseous specimens or solutions in a Cary recording spectrophotometer. Some of the infrared spectra were measured at the Ohio State University in 1953, and some (by courtesy of Professor A. Albert) at the Australian National University in London in 1954—1955, with Perkin-Elmer spectrophotometers (models 12C and 21.)

Manipulations were carried out by vacuum-system methods, and, in the case of the dimer, as quickly as possible in the dark. Trifluoronitrosomethane was prepared and purified as before.²⁵ In a typical preparation of the dimer, the pure nitroso-compound at ~ 0.5 atm. was irradiated in a 1-l. Pyrex bulb, wrapped in orange filter-material between two 500-w tungsten light-bulbs for ~ 1 hr. The dimer was formed almost quantitatively in $\sim 25\%$ yield under these conditions and was readily separated from the nitroso-compound by distillation through traps cooled in melting pentane (since the monomer is too volatile to reflux at -80° in the still available). For preparation on a larger scale a circulatory system is preferable: the monomer is irradiated, the dimer trapped, *e.g.*, at the temperature of melting pentane, and the monomer recycled. The dimer was stored as a solid at low temperatures, and fresh samples were used for each physical measurement.

When irradiated with visible light the dimer became red-brown and inhomogeneous, there was some attack on the glass, and a small amount of non-condensable gas was formed. Shaking the crude product with mercury and dry air to remove nitrogen dioxide gave a grey-black powder containing mercurous oxide, fluoride, nitrite, and nitrate. The separated gas formed more nitrogen dioxide. Distillation in a Fenske-packed still with -80° reflux gave, as first fraction, some white solid subliming at low temperatures (containing carbon dioxide, silicon fluoride, and nitrous oxide), followed by an inseparable mixture of pentafluoro-2-azapropene

²⁷ Petrov and Neimysheva, *J. Gen. Chem. U.S.S.R.*, 1959, **29**, 2135, 2662.

²⁸ Young, Simmons, and Hoffmann, *J. Amer. Chem. Soc.*, 1956, **78**, 5637.

²⁹ Ginsburg, Privezentseva, Shpanskii, Rodionova, Dubov, Khokhlova, Makarov, and Yakubovich, *J. Gen. Chem. U.S.S.R.*, 1960, **30**, 2391.

³⁰ Flournoy, *J. Chem. Phys.*, 1962, **36**, 1106.

and fluoropicrin, identified as in Part VI.³ The nitroamine was detected spectroscopically and not separated. There was also some fluorocarbon material with molecular weight above that of the dimer.

The dimer decomposes in the dark more slowly than in the light to give rather similar products.

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