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Syntheses of Heptafluoronitrosocyclobutane and Nonafluoronitrosocyclopentane and Their Reactions with Tetrafluoroethene, 1,3-Hexafluorobutadiene, and Tetrafluorohydrazine

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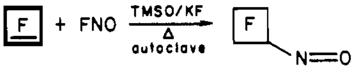
Hexafluorocyclobutene and octafluorocyclopentene were reacted with nitrosyl chloride or nitrogen dioxide in the presence of KF in acetonitrile to give 80% yields of the blue heptafluoronitrosocyclobutane (I) and nonafluoronitrosocyclopentane (II), respectively. Thermal decomposition of I and II in Pyrex glass resulted in the analogous nitro compounds, $CF_2CF_2CF_2CFNO_2$ and $CF_2CF_2CF_2CF_2CFNO_2$. Cycloaddition reactions of I and II with tetrafluoroethene gave the oxazetidines $CF_2CF_2CF_2CFNOCF_2CF_2$ and $CF_2CF_2CF_2CF_2CFNOCF_2CF_2$ and with 1,3-hexafluorobutadiene formed the oxazines $CF_2CF_2CF_2CFNOCF_2CF{=}CFCF_2$ and $CF_2CF_2CF_2CF_2CFNOCF_2CF{=}CFCF_2$. With tetrafluorohydrazine in metal reaction vessels, either I and II or the cycloolefins gave difluoroamines, $CF_2CF_2CF_2CFNF_2$ and $CF_2CF_2CF_2CF_2CFNF_2$. However, in the presence of Pyrex glass, *N*-(heptafluorocyclobutyl)-*N'*-fluorodiimide *N*-oxide and *N*-(nonafluorocyclopentyl)-*N'*-fluorodiimide *N*-oxide ($R_fN(O){=}NF$) resulted from heating I and II with N_2F_4.

Introduction

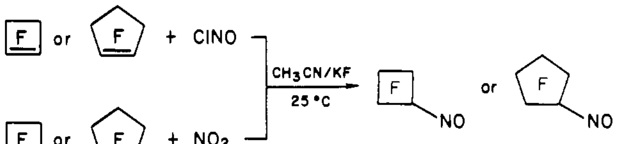
The chemistry and reactions of nitrosofluoroalkanes, particularly for CF_3NO, have been a fertile field for much exciting work by synthetic and physical chemists alike. Although originally identified in 1936 as a product from the reaction of fluorine with a mixture of silver cyanide and silver nitrate,[2] it was only with the invention of perfluoroalkyl iodides (R_fI) that R_fNO could be obtained in reasonable yields.[3] Thirty years later the reactions of these blue compounds continue to be studied and, in fact, currently CF_3NO is receiving considerable attention as a precursor for the introduction of trifluoromethyl groups into primarily aromatic systems.[4-6] While a rather large number of acyclic nitrosofluoroalkanes have been synthesized, only a few fluoroaromatic nitroso compounds and only one cyclic nitrosofluoroalkane are known. The latter, heptafluoronitrosocyclobutane, was first reported as a product of the addition of nitrosyl fluoride to hexafluorocyclobutene[7]



73%

but little spectral evidence was given and apparently no reaction chemistry was attempted.

In our hands, the above synthesis gave much lower yields of the cyclic nitroso compound and was inconvenient because of the necessity for synthesizing the nitrosyl fluoride on a rather large scale followed by its transfer to the reaction mixture. Thus, in this paper we describe one-pot syntheses[8] of heptafluoronitrosocyclobutane and nonafluoronitrosocyclopentane in excellent yields via the in situ generation of FNO, viz.:



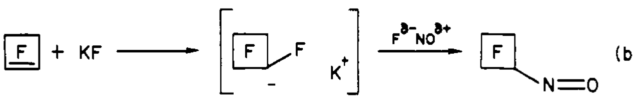
I (80%) II (80%)

Additionally, these two nitroso compounds have been thoroughly characterized, and their reaction chemistry has been studied. In spite of the higher degree of strain of the cyclobutyl ring, the behaviors of I and II are essentially identical and also very similar to that of CF_3NO.

Results and Discussion

There are a variety of synthetic routes to nitrosyl fluoride including the direct fluorination of NO with elemental fluorine[9] and the fluorination of NO_2 with an alkali-metal fluoride,[10] but the former synthesis requires the subsequent transfer of the product FNO to the reaction vessel that contains the solvent, the olefin, and the alkali-metal fluoride. Thus, we elected to generate the FNO required for the synthesis of cyclic nitroso compounds in situ[8] by adding all of the reactants to a Pyrex glass reaction vessel and allowing the mixture to be stirred for an extended period. When millimolar amounts of ClNO are added to an excess of anhydrous KF in a small amount of CH_3CN, the yellow color of the ClNO is discharged in about 4 h, and after this time, the then colorless contents of the vessel turn blue slowly over a period of several days if an olefin is added. The rate of addition of FNO to the olefin appears to be directly related to the amount of solvent present. This leads us to believe that the reaction occurs stepwise

$$KF + ClNO \xrightarrow[25\,°C/4\ h]{CH_3CN} KCl + FNO \qquad (a)$$



even though all reactants are condensed into the vessel that contains the KF at −196 °C. If the ClNO is not converted completely to FNO prior to the addition of the olefin, very small amounts of the chloro cyclic nitroso compound are formed on the basis of mass spectral evidence. For the case of NO_2, the reaction is one where NO_2 is converted quanti-

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[1] American Association of University Women International Fellow, 1982–1983.

[2] Ruff, O.; Giese, M. *Ber. Dtsch. Chem. Ges. B* **1936**, *69*, 598, 684.

[3] Henry, M. C.; Griffis, C. G.; Stump, E. C. *Fluorine Chem. Rev.* **1967**, *1*, 1.

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tatively to FNO and alkali-metal nitrate.[10] These methods involving in situ generation of FNO are definitely superior to other routes because of the high yields of I and II obtained. The presence of the alkali-metal fluoride precludes glass attack by FNO, which allows the reactions to proceed in Pyrex vessels. Separation of II from acetonitrile is difficult by trap-to-trap fractionation, and for absolute purity of the nitroso compound, gas chromatography must be employed. However, this is not necessary for studying the reaction chemistry of these materials.

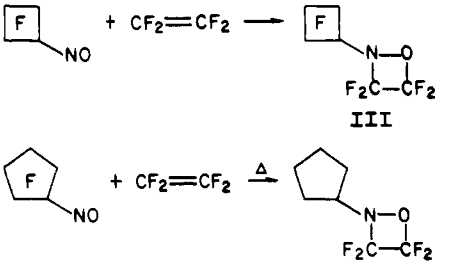
Although trifluoronitrosomethane is easily dimerized even in diffuse light through Pyrex glass, both I and II are found to be stable.[11]

$$\underset{\text{blue}}{2CF_3NO} \xrightarrow{h\nu} \underset{\text{yellow}}{(CF_3)_2NONO}$$

However, decomposition occurs upon ultraviolet irradiation in quartz. Thermolysis at 55 °C for 2 days or at 165 °C for 1 h in Pyrex glass gave the colorless nitro derivatives as major products. The infrared spectra of the nitro compounds are characterized by ν_{NO_2} bands at 1614 and 1627 cm^{-1} for the four- and five-membered rings, respectively. Trifluoronitromethane as well as $CF_3N{=}NCF_3$ and $CF_3N{=}CF_2$ are thermal decomposition products of CF_3NO.[12,13]

These cyclic nitroso compounds are deep blue, and strong bands assigned to ν_{NO} occur at 1593 and 1606 cm^{-1} for I and II, respectively. In the ^{19}F NMR spectrum, the fluorine atom that is geminal to the nitroso group is characteristically shifted upfield in the region ϕ −160 to −180. The UV spectra of I and II show λ_{max} at 659 nm (ϵ = 6.3) and 654 nm (ϵ = 9.6), respectively, due to the n → π* transition. II also exhibits some fine structure between λ 371 and 323 nm.

1,2-Cycloaddition reactions occur when either cyclic nitroso compound is heated at 55–60 °C with C_2F_4 to form the oxazetidines[14,15] in about 10% yield.

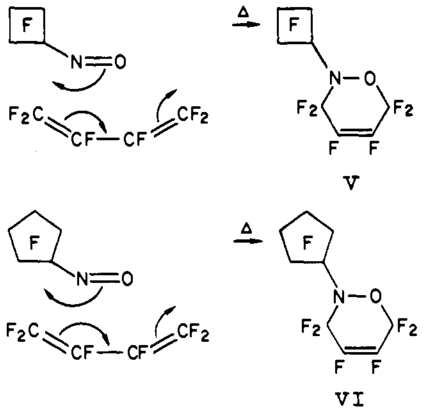


III

IV

A major portion of the products was found as nonvolatile polymeric materials and was not characterized. In the infrared spectra of III and IV, bands at 1415 and 1425 cm^{-1} are assigned to ν_{NO}. The ^{19}F NMR spectra are characteristic, with some second-order effects being observed for III. In view of these cycloadditions, an attempt was made to isolate oxazetidines that could result from interaction of each of the nitroso compounds with its parent cyclic olefin. None was found.

With 1,3-hexafluorobutadiene, the cyclic nitroso compounds undergo Diels–Alder 1,4-cycloaddition reactions to form the oxazines[16,17] in 35% yield as well as unidentified polymeric materials.

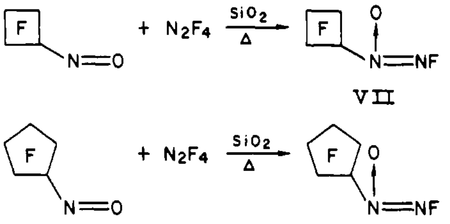


V

VI

Stretching frequencies for the olefinic double bonds in V and VI appear at 1767 and 1772 cm^{-1}, respectively. No other simple cycloaddition compounds, e.g., oxazetidines, were isolated.

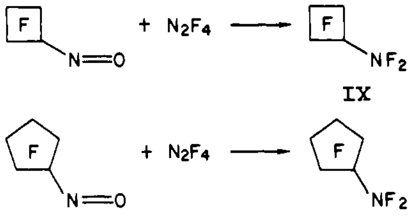
The first examples of perfluorocycloalkyl-*N*′-fluorodiimide *N*-oxides were formed when the nitroso compounds were heated with tetrafluorohydrazine in the presence of finely divided Pyrex glass.



VII

VIII

When the same reactions were carried out in the absence of glass, no *N*′-fluorodiimide *N*-oxide formation was observed, but rather (heptafluorocyclobutyl)difluoramine (IX) and (nonafluorocyclopentyl)difluoramine (X) resulted in low yield.



IX

X

Compounds IX and X were also synthesized in higher yields by the ultraviolet irradiation of hexafluorocyclobutene or

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octafluorocyclopentene with N_2F_4 in a quartz vessel. No reaction occurred if the cycloolefin/N_2F_4 mixture was heated at 110 °C for 10 h although it is claimed that ring opening occurred with the cyclobutene to form 1,4-bis(difluoroamine)hexafluorobut-2-ene.[18]

All of the new compounds are stable at 25 °C and are hydrolytically stable, at least in moist air. A molecular ion is observed in the mass spectra of compounds I–X.

Experimental Section

Materials. All reagents were used as received from commercial suppliers without further purification. Sources were as follows: hexafluorocyclobutene, octafluorocyclopentene, hexafluorobutadiene, and tetrafluoroethene, PCR; nitrosyl chloride, Matheson; tetrafluorohydrazine, Air Products.

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex glass vacuum system equipped with a Heise–Bourdon tube gauge and a Televac thermocouple gauge. Most of the starting materials and products were measured quantitatively by using *PVT* techniques. Products were purified by fractional condensation (trap-to-trap distillation).

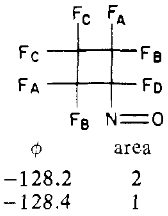
Heptafluoronitrosocyclobutane and nonafluoronitrosocyclopentane could be completely purified on a Varian Aerograph Model A-700 or Hewlett-Packard 5710A gas chromatograph equipped with Valco gas sample injection values. The separation was done on 11 ft × $^1/_4$ in. columns (containing 25% w/w Kel-F oil No. 3 on Chromosorb P), at room temperature, with an injection and detector temperature of 100 °C.

Photolysis reactions were accomplished by using a Hanovia utility ultraviolet quartz lamp. Infrared spectra were recorded with a Perkin-Elmer 599 spectrometer by using a 10-cm cell equipped with KBr windows. UV data were obtained on a Beckman Spectrophotometer Acta MVII equipped with a cell of 1-cm path length. ^{19}F NMR spectra were obtained on either a JEOL FX-90Q Fourier transform spectrometer operating at 84.26 MHz or a Varian EM-360L spectrometer operating at 54.6 MHz by using $CDCl_3$ and/or $CFCl_3$ as a solvent and $CFCl_3$ as an internal or external reference. Chemical shifts upfield of the reference are assigned negative values. Mass spectra were recorded with a Hitachi Perkin-Elmer RMU-6E spectrometer operating at 17 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

Slush baths were made as follows: −98 °C, methanol–liquid N_2; −78 °C, ethanol–dry ice; −60 °C, 4:1 ratio of $EtOH/H_2O$ (by volume)–liquid N_2; −35 °C, 4:3 ratio of $EtOH/H_2O$ (by volume)–liquid N_2. The KF was finely powdered and dried at 160 °C for a number of days prior to use. When used, it was put into warm Pyrex glass flasks to ensure that the KF remained dry.

Reactions of Fluorocycloolefins with ClNO. To a warm 1-L round-bottomed Pyrex glass flask equipped with a Kontes Teflon stopcock and a Teflon-coated stirring bar was added about 10 g (170 mmol) of powdered anhydrous KF. The flask was evacuated, and ~25 mmol of CH_3CN, 15 mmol of fluorocycloolefin, and 25 mmol of ClNO were condensed in at −196 °C. The flask was allowed to warm to room temperature and the reaction mixture stirred on a magnetic plate for about 7–10 days, or until no fluorocycloolefin remained as determined by infrared spectroscopy. After trap-to-trap distillation, the trap at −98 °C contained the blue fluoronitrosocycloalkane, which had passed through a trap at −78 °C.

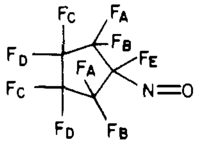
Properties of Heptafluoronitrosocyclobutane, $CF_2CF_2CF_2CFNO$ (I). The compound was obtained in a yield of ~80%. The infrared spectrum shows 1593 (s), 1412 (s), 1342 (s), 1310 (sh), 1280 (vs)8, 1230 (vs), 1070 (sh), 1014 (vs), 940 (vs), 892 (m), 753 (m)8, 627 (m), and 574 (s) cm^{-1}. The UV spectrum was obtained by dissolving 0.5 mmol of the nitroso compound into 3 mL of $CHCl_3$. λ_{max} was formed at 659 nm with ϵ 6.3 cm^{-1} mol^{-1} L. The ^{19}F NMR spectrum consists of multiplets with the following chemical shifts and area ratios:



area		ϕ	area		ϕ
2	F_A	−128.2	2	F_C	−131.5
2	F_B	−128.4	1	F_D	−173.3

The mass spectrum shows a molecular ion at *m/e* 211 ($C_4F_7NO^+$). Other principal peaks were observed at *m/e* 181 ($C_4F_7^+$), 150 ($C_3F_6^+$), 100 ($C_2F_4^+$), and 30 (NO^+).

Properties of Nonafluoronitrosocyclopentane, $CF_2CF_2CF_2CF_2CFNO$ (II). The compound was obtained in a yield of ~80%. The infrared spectrum shows 1606 (ms), 1360 (sh), 1322 (s), 1276 (ms), 1230 (vs), 1026 (s), 980 (vs), 884 (m), 633 (m), and 605 (m) cm^{-1}. The UV spectrum was obtained by dissolving 0.5 mmol of the nitroso compound in 3 mL of $CHCl_3$. λ_{max} was observed at 654 nm with ϵ 9.6 cm^{-1} mol^{-1} L. The mass spectrum shows a molecular ion at *m/e* 261 ($C_5F_9NO^+$). Other principal peaks are observed at *m/e* 231 ($C_5F_9^+$), 200 ($C_4F_8^+$) 150 ($C_3F_6^+$), 100 ($C_2F_4^+$), and 30 (NO^+). The ^{19}F NMR spectrum consists of multiplets with the following chemical shifts, coupling constants, and area ratios:



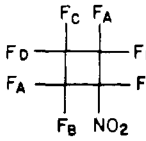
area		ϕ	
4	F_A	−123.5	$J = 270$ Hz
	F_B	−131.1	
	F_C	−128.	$J = 260$ Hz
	F_D	−132.1	
	F_E	−175.2 (s)	

Reactions of Fluorocycloolefins with FNO. To a warm 75-mL stainless-steel Hoke cylinder fitted with a stainless-steel Hoke valve and containing ~5 g (86 mmol) of dry KF, 10 mL of tetramethylene sulfone, and 3 stainless-steel ball bearings was added 10 mmol of fluorocycloolefin and 15 mmol of FNO. The cylinder was allowed to warm to room temperature over a period of about 4 h and then heated at 55 °C for 36 h. It was then shaken vigorously for 3 days on a paint shaker.

Trap-to-trap distillation of the reaction mixture gave a 40% yield of heptafluoronitrosocyclobutane (I), and in the case of nonafluoronitrosocyclopentane (II), a 50% yield was found. A green less volatile material was seen as a byproduct in the latter reaction, but this was not identified.

Thermolysis of I. To a 30 mL thick-walled Pyrex reaction tube was added 6 mmol of I. The tube was sealed and heated in an oven at 165 °C for 1 h. After removal of the noncondensable materials, trap-to-trap distillation gave an ~30% yield of colorless $CF_2CF_2CF_2CFNO_2$ in the trap at −78 °C after having passed through a trap at −55 °C. An unidentified pale green involatile liquid remained in the reaction tube. A large amount of SiF_4 was also generated in the reaction.

Properties of Heptafluoronitrocyclobutane, $CF_2CF_2CF_2CFNO_2$. The infrared spectrum shows 1614 (vs), 1411 (m), 1353 (ms), 1322 (s), 1274 (s), 1240 (vs), 1081 (ms), 1009 (ms), 965 (s), 942 (s), 905 (w), 807 (s), 780 (w), 691 (w), 644 (w), and 556 (w) cm^{-1}. The mass spectrum does not show a molecular ion peak but has peaks at *m/e* 211 ($C_4F_7ON^+$), 181 ($C_4F_7^+$), 162 ($C_4F_6^+$), 131 ($C_3F_5^+$), 100 ($C_2F_4^+$), 69 (CF_3^+), 46 (NO_2^+), and 30 (NO^+). The ^{19}F NMR spectrum consists of multiplets with the following chemical shifts, coupling constants, and area ratios:



area		ϕ	
4	F_A	−126.3	$J = 202.5$ Hz
	F_B	−129.3	
2	F_C	−129.7	$J = 202.5$ Hz
	F_D	−133.8	
1	F_E	−147.2 (s)	

Anal. Calcd for $C_4F_7O_2N$: C, 21.14; F, 58.6. Found: C, 21.20; F, 60.8.

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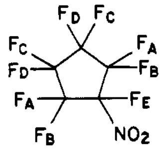
Thermolysis of II. To a 30 mL thick-walled Pyrex reaction tube was added 5 mmol of nonafluoronitrosocyclopentane. The sealed tube was heated in an oven at 165 °C for 40 min. After the removal of noncondensable gases, trap-to-trap distillation gave colorless nonafluoronitrocyclopentane in ~35% yield in the trap at −78 °C after having passed through a trap at −55 °C.

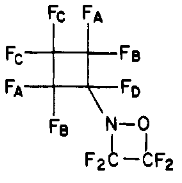
Properties of Nonafluoronitrocyclopentane, $CF_2CF_2CF_2CF_2CFNO_2$. The infrared spectrum shows 1627 (vs), 1316 (s), 1281 (m), 1235 (vs), 1043 (m), 995 (vs), 972 (m), 941 (w), 808 (m), 670 (vw), 635 (vs), 598 (vw), and 564 (w) cm^{-1}. The mass spectrum does not show a molecular ion peak, but a peak at *m/e* 231 ($C_5F_9^+$) due to the loss of NO_2 is seen. Other prominent peaks are observed at *m/e* 212 ($C_5F_8^+$), 181 ($C_4F_7^+$), 162 ($C_4F_6^+$), 131 ($C_3F_5^+$), 100 ($C_2F_4^+$), 69 (CF_3^+), 46 (NO_2^+), and 30 (NO^+). The ^{19}F NMR spectrum is an AB pattern that has the following shifts, coupling constants, and area ratios:



area		ϕ	
4	F_A	−121.71	$J = 259$ Hz
	F_B	−126.52	
4	F_C	−124.6	$J = 292$ Hz
	F_D	−128.2	
1	F_E	−146.2 (s)	

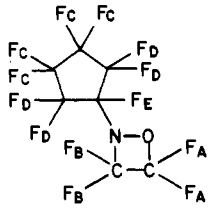
Reactions of Fluoronitrosocycloalkanes with $CF_2{=}CF_2$. A 2-mmol portion of a fluoronitrosocycloalkane and 3 mmol of $CF_2{=}CF_2$ were condensed into a Pyrex glass tube equipped with a Kontes Teflon stopcock. The reaction mixture was allowed to come to room temperature and then heated to 55–60 °C by using a Thermolyne Briskheat flexible electric heating tape. It is important to maintain the tube in a horizontal position to ensure uniform heating. After approximately 2 days of heating (or until no blue color remains), vacuum distillation gives a colorless liquid in a trap at −60 °C after having passed through a trap at −45 °C. A large amount of involatile colorless polymeric material remains in the reaction vessel.

(a) Properties of (Heptafluorocyclobutyl)oxazetidine, $CF_2CF_2CF_2CFNOCF_2CF_2$ (III). The colorless oxazetidine monomer was found in 10% yield. The infrared spectrum shows 1415 (s), 1318 (vs), 1268 (br, vs), 1242 (br, vs), 1213 (sh), 1071 (s), 1010 (s), 951 (vs), 912 (vs), 890 (sh, s), 694 (vw), 643 (w), 579 (s), and 574 (vw) cm^{-1}. The mass spectrum contains a molecular ion at *m/e* 311 ($C_6F_{11}ON^+$). Other prominent peaks are observed at *m/e* 245 ($C_5F_9N^+$), 211 ($C_4F_7ON^+$), 181 ($C_4F_7^+$), 150 ($C_3F_6^+$), 145 ($C_3F_5N^+$), 100 ($C_2F_4^+$), 66 (OCF_2^+), and 64 (NCF_2^+). The ^{19}F NMR spectrum shows an AB pattern with the following chemical shifts, coupling constants, and area ratios:



area		ϕ	
2	F_{CF_2O}	−83.4	
2	F_{CF_2N}	−98.5	
4	F_A	−127.3	$J = 226$ Hz
	F_B	−133.1	
2	F_C	−129.6	
2	F_D	−167.5	

(b) Properties of (Nonafluorocyclopentane)oxazetidine, $CF_2CF_2CF_2CF_2CFNOCF_2CF_2$ (IV). The colorless oxazetidine monomer was formed in yields of about 10%. The infrared spectrum is as follows: 1618 (s, $CF_2CF_2CF_2CF_2CFNO_2$ impurity), 1425 (s), 1365 (ms), 1312 (s), 1225 (vs), 1180 (s), 1152 (s), 1020 (br, ms), 992 (vs), 971 (sh), 908 (m), 860 (m), 800 (m), 788 (m), 750 (m), 702 (w), 673 (w), 610 (w), 556 (w), 509 (w), 448 (w) cm^{-1}. The mass spectrum contains a molecular ion peak at *m/e* 361 ($C_7F_{13}ON^+$). Other prominent peaks are seen at *m/e* 295 ($C_6F_{11}N^+$), 261 ($C_5F_9ON^+$), 231 ($C_5F_9^+$), 150 ($C_3F_6^+$), 145 ($C_3F_5N^+$), 100 ($C_2F_4^+$), 66 (OCF_2^+), and 64 (NCF_2^+). The ^{19}F NMR spectrum consists of multiplets with the following shifts, coupling constants, and area ratios:

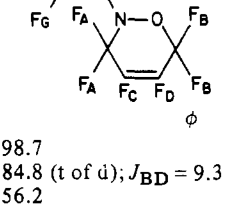


area		ϕ
2	F_A	−84 (s)
2	F_B	−96 (d); $J_{BE} = 19.5$ Hz
4	F_C	−126 (s)
4	F_D	−134 (s)
1	F_E	−163 (t)

Anal. Calcd for $C_7F_{13}ON$: C, 23.28; F, 68.4. Found: C, 23.37; F, 68.0.

Reaction of Fluoronitrosocycloalkanes with $CF_2{=}CFCF{=}CF_2$. A 6-mmol portion of a fluoronitrosocycloalkane and 8 mmol of $CF_2{=}CF{-}CF{=}CF_2$ were condensed into a Pyrex glass tube equipped with a Kontes Teflon stopcock. The reaction mixture was allowed to come to room temperature and was then heated to 55–60 °C by using a Thermolyne briskheat flexible electric heating tape. The tube was held in a horizontal position during the reaction to ensure uniform heating. After heating for 14 h, the reaction mixture was vacuum distilled, and a 35% yield of the colorless oxazine was found in the trap at −60 °C, having passed through a trap at −35 °C. A polymeric material remained on the walls of the reaction tube.

(a) Properties of (Heptafluorocyclobutane)oxazine, $CF_2CF_2CF_2CFNOCF_2CF{=}CFCF_2$ (V). The infrared spectrum shows 1767 (s), 1417 (m), 1379 (vs), 1312 (s), 1300 (s), 1272 (s), 1252 (vs), 1246 (vs), 1211 (vs) 1188 (vs), 1168 (vs), 1145 (vs), 1095 (w), 1040 (s), 992 (w), 955 (vs), 930 (vs), 879 (vw), 782 (s), 743 (s), 690 (w), 625 (w), 607 (m), 582 (m), 565 (s), 520 (m), and 420 (w) cm^{-1}. The mass spectrum shows a molecular ion peak M^+ at *m/e* 373 ($C_8F_{13}ON^+$). Other prominent peaks were seen at *m/e* 354 ($C_8F_{12}ON^+$), 273 ($C_6F_9ON^+$), 242 ($C_5F_8ON^+$), 181 ($C_4F_7^+$), 162 ($C_4F_6^+$), 131 ($C_3F_5^+$), 112 ($C_3F_4^+$), 100 ($C_2F_4^+$), and 69 (CF_3^+). The ^{19}F NMR spectrum consists of multiplets with the following chemial shifts, coupling constants, and area ratios:

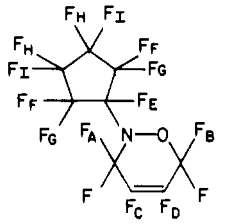


area		ϕ	
2	F_A	−98.7	
2	F_B	−84.8 (t of d); $J_{BD} = 9.3$ Hz, $J_{BA} = 3.7$ Hz	
1	F_C	−156.2	
1	F_D	−154.8	
1	F_E	−161.2	
4	F_F	−126.9	$J = 225$ Hz
	F_G	−132.6	
2	F_H	−129.1	$J = 225$ Hz
	F_I	−133.1	

Anal. Calcd for $C_8F_{13}ON$: C, 25.75; F, 66.2. Found: C, 25.34; F, 66.0.

(b) Properties of (Nonafluorocyclopentane)oxazine, $CF_2CF_2CF_2CF_2CFNOCF_2CF{=}CFCF_2$ (VI). The infrared spectrum shows

1772 (s), 1378 (vs), 1319 (s), 1269 (s), 1229 (vs), 1212 (vs), 1181 (s), 1170 (s), 1150 (s), 1032 (m), 1001 (w), 973 (s), 955 (m), 935 (m), 780 (w)8 742 (w), 729 (m), 607 (vw), 593 (vw)8 566 (w), and 520 (w) cm^{-1}. The mass spectrum shows a molecular ion peak M$^+$ at *m/e* 423 ($C_9F_{15}ON^+$)9 Other prominent peaks were seen at *m/e* 404 ($C_9F_{14}ON^+$), 338 ($C_8F_{12}N^+$), 162 ($C_4F_6^+$), 131 ($C_3F_5^+$), and 100 ($C_2F_4^+$). The ^{19}F NMR spectrum consists of multiplets with the following chemical shifts, coupling constants, and area ratios:

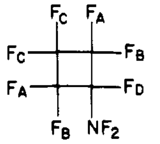


area		ϕ	
2	F_A	−96.7	
2	F_B	−85.7	
1	F_C	−155.7	
1	F_D	−155.2	
1	F_E	−155.8 (s)	
2	F_F	−118.6	$J = 257$ Hz
	F_G	−132.1	
2	F_H	−124.5	$J = 257$ Hz
	F_I	−130.8	

Anal. Calcd for $C_9F_{15}ON$: C, 25.56; F, 67.35. Found: C, 25.59; F, 67.40.

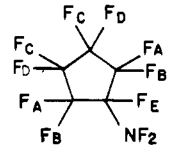
Photolysis of Fluorocycloalkenes with N_2F_4 in Quartz. To a 300-mL quartz reaction vessel equipped with a Kontes Teflon stopcock were added 3 mmol of a fluorocycloalkene and 6 mmol of N_2F_4. After it was warmed from −196 °C to room temperature over a period of 1 h, the reactionv essel was placed about 60 cm from the UV lamp.

(a) Properties of (Heptafluorocyclobutyl)difluoramine, $\overline{\mathrm{CF_2CF_2CF_2C}}\mathrm{FNF_2}$ (IX). After 36 h of photolysis, trap-to-trap distillation gives an 86% yield of colorless (heptafluorocyclobutyl)difluoramine in the trap at −98 °C after having passed through a trap at −78 °C. The infrared spectrum is 1412 (m), 1312 (s), 1287 (s), 1235 (vs), 1178 (m), 1150 (m), 1009 (m), 978 (s), 939 (vs), 915 (s), 890 (sh), 830 (w), 783 (m), 740 (w), 686 (w), 620 (m), 582 (m), and 523 (w) cm^{-1}. A molecular ion at *m/e* 233 ($C_4F_9N^+$) is observed in the mass spectrum. Other prominent peaks were seen at *m/e* 214 ($C_4F_8N^+$), 195 ($C_4F_7N^+$), and 181 ($C_4F_7^+$). The ^{19}F NMR spectrum consists of multiplets with the following chemical shifts, coupling constants, and area ratios:



area		ϕ
2	NF_2	+22.4 (br s)
2	F_A	−129.8 (d); $J_{AB} = 12.8$ Hz
2	F_B	−129.9 (d)
2	F_C	−132.4 (s)
1	F_D	−182.1 (t); $J_{D\text{-}NF_2} = 12.2$ Hz

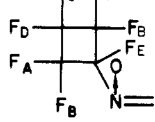
(b) Properties of (Nonafluorocyclopentyl)difluoramine, $\overline{\mathrm{CF_2CF_2CF_2CF_2C}}\mathrm{FNF_2}$ (X). After 30 h of photolysis, trap-to-trap distillation gave an 80% yield of (nonafluorocyclopentyl)difluormaine in the trap at −78 °C, having passed through a trap at −60 °C. Gas-phase chromatography was necessary to obtain the pure compound. The infrared spectrum shows 1360 (m), 1318 (s), 1280 (ms), 1225 (vs), 1055 (m), 1020 (ms), 1000 (vs), 950 (vs), 886 (s), 775 (ms), 670 (w), 612 (m), 570 (w), 550 (w), and 526 (w) cm^{-1}. A molecular ion peak at *m/e* 283 ($C_5F_{11}N^+$) was observed in the mass spectrum. Other prominent peaks are seen at *m/e* 264 ($C_5F_{11}N^+$) was observed in the mass spectrum. Other prominent peaks are seen at *m/e* 264 ($C_5F_{10}N^+$), 250 ($C_5F_{10}^+$), 231 ($C_5F_9^+$), 212 ($C_5F_8^+$), 193 ($C_5F_7^+$), 181 ($C_4F_7^+$), and 162 ($C_4F_6^+$). The ^{19}F NMR spectrum consists of multiplets with the following chemical shifts, coupling constants, and area ratios:



area		ϕ	
2	NF_2	+21.4 (br s)	
2	F_A	−124.4	$J = 268$ Hz
2	F_B	−131.6	
2	F_C	−129.2	$J = 254$ Hz
2	F_D	−133.5	
1	F_E	−174.4	

Thermolysis of Fluoronitrosocycloalkanes in the Presence of Glass and N_2F_4. Crushed Pyrex glass (~20 g) was placed into a 75-mL stainless-steel Hoke cylinder fitted with a stainless-steel Hoke valve. A 2-mmol portion of the fluoronitrosocycloalkane and 4 mmol of N_2F_4 were condensed into the cylinder, which was then allowed to warm to room temperature over a period of 12 h. The cylinder was then heated at 55 °C for 16 h.

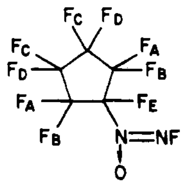
(a) Properties of *N*-(Heptafluorocyclobutyl)-*N'*-fluorodiimide *N*-Oxide, $\overline{\mathrm{CF_2CF_2CF_2C}}\mathrm{FN(O)NF}$ (VII). Trap-to-trap distillation gave a 50% yield of the colorless compound in the trap at −78 °C, having passed through a trap at −50 °C. The distillation was repeated to ensure a pure compound. The infrared spectrum is as follows: 1616 (m), 1522 (vs), 1415 (s), 1320 (vs), 1298 (sh), 1242 (vs), 1157 (m), 1052 (m), 1009 (m), 970 (vs), 860 (w), 833 (vs), 690 (w), 631 (m), 589 (m), 558 (m) cm^{-1}. The mass spectrum shows a molecular ion peak at *m/e* 244 ($C_4F_8N_2O^+$) with other prominent peaks at *m/e* 211 ($C_4F_7NO^+$), 181 ($C_4F_7^+$), 150 ($C_3F_6^+$), 131 ($C_3F_5^+$), 100 ($C_2F_4^+$), 81 ($C_2F_3^+$), 69 (CF_3^+), 63 (N_2FO^+), 47 (N_2F^+), and 30 (NO^+). The ^{19}F NMR spectrum consists of multiplets with the following chemical shifts, coupling constants, and area ratios:



area		ϕ	
4	F_A	−125.0	$J = 232$ Hz
	F_B	−129.2	
2	F_C	−128.7	$J = 224$ Hz
	F_D	−131.7	
1	F_E	−154.6 (s)	
1	F_F	+57.4 (br s)	

Anal. Calcd for $C_4F_8ON_2$: C, 1968; F, 62.28. Found: C, 19.68; F, 62.1.

(b) Properties of *N*-(Nonafluorocyclopentyl)-*N'*-fluorodiimide *N*-Oxide, $\overline{\mathrm{CF_2CF_2CF_2CF_2C}}\mathrm{FN(O)NF}$ (VIII). Trap-to-trap distillation gave a 25% yield of the colorless compound in the trap at −55 °C after having passed through a trap at −30 °C. The infrared spectrum shows 1630 (w), 1625 (sh), 1530 (s), 1350 (sh), 1318 (s), 1263 (sh), 1236 (vs), 1179 (w), 1038 (vs), 992 (vs), 850 (m), 817 (vs), 703 (vw), 672 (vw), 627 (w), 595 (m), and 560 (w) cm^{-1}. The mass spectrum shows a molecular ion peak at *m/e* 294 ($C_5F_{10}ON_2^+$). Other prominent peaks were seen at *m/e* 261 ($C_5F_9ON^+$), 231 ($C_5F_9^+$), 181 ($C_4F_7^+$), 131 ($C_3F_5^+$), and 69 (CF_3^+). The ^{19}F NMR spectrum is second order and shows the characteristic broad singlet at ϕ +58.4 due to the fluorine atom bonded to the nitrogen atom and a singlet at ϕ −149 due to the fluorine atom geminal to the azoxy group.



area		ϕ
4	F_A	-120.76 } $J = 264$ Hz
	F_B	-130.25
4	F_C	-124.1 } $J = 253$ Hz
	F_D	-129.0
1	F_E	-149.7 (s)
1	F_F	$+58.4$ (br s)

Reactions of Heptafluoronitrosocyclobutane with N_2F_4 in Metal. Into a 75-mL stainless-steel Hoke cylinder fitted with a stainless-steel Hoke valve were added 4 mmol of $\overline{CF_2CF_2CF_2CF}NO$ and 8 mmol of N_2F_4. The cylinder was allowed to warm to and remain at room temperature for 12 h. After it was heated for 3 h at 45 °C, spectroscopic examination of the products obtained after trap-to-trap distillation showed that (heptafluorocyclobutyl)difluoramine is formed in about 30% yield. In a similar reaction between nonafluoronitrosocyclopentane and N_2F_4, (nonafluorocyclopentyl)difluoramine was found in about 30% yield.

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Registry No. I, 2261-41-8; II, 91816-92-1; III, 91816-93-2; IV, 91816-94-3; V, 91816-95-4; VI, 91816-96-5; VII, 91816-97-6; VIII, 91816-98-7; IX, 91816-99-8; X, 91817-00-4; $CF_2{=}CF_2$, 116-14-3; $CF_2{=}CFCF{=}CF_2$, 685-63-2; N_2F_4, 10036-47-2; hexafluorocyclobutene, 697-11-0; octafluorocyclopentene, 559-40-0.

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Molecular Structure of Diaminotrifluorophosphorane, $PF_3(NH_2)_2$, in the Gas Phase

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The gas-phase molecular structure of $PF_3(NH_2)_2$ at 50 °C has been determined by electron diffraction. The heavy-atom skeleton is a trigonal bipyramid of C_{2v} symmetry with the nitrogen atoms occupying equatorial sites. The N–P–N angle is larger than the other equatorial angles, and the axial P–F bonds are bent slightly toward the equatorial fluorine atom. The planes of the $-NH_2$ groups are perpendicular to the equatorial plane of the molecule. There is no evidence for nonplanarity of the $-PNH_2$ groups, but small deviations from planarity cannot be excluded. Values of the principal structural parameters with estimated 2σ uncertainties (obtained after taking the effects of vibrational averaging into account) are $\langle r_g(\text{P–Y})\rangle$ (weighted average phosphorus bond length) = 1.616 (4) Å, $\Delta r_g(\text{P–N,F}_e)$ (difference in equatorial bond lengths) = 0.088 (22) Å, $\Delta r_g(\text{P–F}_a\text{,F}_e)$ = 0.060 (8) Å, $r_g(\text{P–F}_e)$ = 1.560 (10) Å, $r_g(\text{P–N})$ = 1.648 (13) Å, $r_g(\text{P–F}_a)$ = 1.619 (7) Å, $r_g(\text{N–H})$ = 1.033 (10) Å, $\angle\text{N–P–F}_e$ = 116.3 (5)°, $\angle\text{F}_a\text{–P–F}_e$ = 89.5 (9)°, and $\angle\text{P–N–H}$ = 119.8 (22)°. A rough value for the twofold torsional barrier of the $-NH_2$ groups, obtained from the torsional amplitude, is 13 kcal·mol^{-1}, in good agreement with NMR measurements. $PF_3(NH_2)_2$ is discussed with the aid of comparison to the structures of other fluorophosphoranes.

Introduction

Pentacoordinate phosphorus compounds play an important role in the development and understanding of main-group stereochemistry. Thus, the structure, vibrational force field, and internal dynamics of PF_5 have been extensively investigated both experimentally and theoretically,[2] and much elegant work has been recently done on complex phosphoranes with cyclic substituents,[3] which have structures ranging from distorted trigonal bipyramidal to square pyramidal. It is surprising, therefore, that relatively little precise structural information is available for simple phosphoranes. Derivatives of PF_5, for example, offer sensitive tests of the usefulness of bonding theories, be they as simple as VSEPR[4] or as involved as ab initio calculations, for description and prediction of structural variation in these rather flexible molecules.

We have recently begun a series of studies of the gas-phase structure of phosphoranes that is planned to include halides, amines, and hydrides. This article presents our results for diaminofluorophosphorane.

Experimental Section

A sample of $PF_3(NH_2)_2$ was prepared as follows.

To a 1-L Pyrex round-bottomed flask equipped with a cold finger and a Kontes Teflon stopcock was added 15 mmol of PF_5. Anhydrous NH_3 (45 mmol) was added very slowly to the flask by maintaining a slightly higher pressure of NH_3 in the vacuum line than the pressure of PF_5 in the flask. The reaction was rapid and exothermic. A dense cloud formed immediately on contact. After all of the NH_3 was added, the mixture was kept at 25 °C for 0.25 h and then condensed in the cold finger at −196 °C. As the contents were allowed to warm slowly to 25 °C the volatile material was caused to move under dynamic vacuum into and through a trap cooled to −45 °C. The pure compound, $PF_3(NH_2)_2$ (40%), was retained in this trap. Prior to reaction the entire vacuum system and reaction vessel had been carefully dried. The purity of $PF_3(NH_2)_2$ was confirmed by infrared and ^{19}F and ^{31}P NMR spectral measurements. These spectra agreed with those in the literature.[5]

Diffraction photographs were made in the Oregon State apparatus under the following conditions: r^3 sector; nozzle-tip temperature, 50 °C; bulk sample temperature, 45–55 °C; plates, 8 × 10 in. Kodak projector slide medium contrast; development, 10 min in D-19 diluted 1:1; nominal nozzle-to-plate distances, 75 and 30 cm; exposure times, 150–300 s; nominal electron wavelengths, 0.057 Å (calibrated from CO_2 with $r_a(\text{CO})$ = 1.1646 Å, $r(\text{O·O})$ = 2.3244 Å); number of plates

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[2] For a review of PF_5 and its derivatives see: Holmes, R. R. *ACS Monogr.* **1980**, *No. 175*; **1980**, *No. 176*.

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[5] Lustig, M.; Roesky, H. W. *Inorg. Chem.* **1970**, *9*, 1289.

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