

Central Research Laboratories
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Organic Fluoronitrogens. IV. Halo-Diazirines (I)

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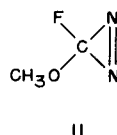
The physical and spectral properties of five previously undisclosed diazirines substituted with electron-withdrawing groups are described. The halo-diazirines yield the respective divalent carbon species and nitrogen on pyrolysis. The cyanofluoro-, fluoromethoxy- and fluorodifluoramino-carbenes form the respective cyclopropanes with tetrafluoroethylene. The intramolecular reactions of difluoramino-substituted carbenes are also discussed. The ultraviolet spectra are presented.

Since the disclosure of the hydrocarbon diazirines (2) in 1960, this class of compounds has attracted considerable interest as indicated by the number of publications in the field. However, except for difluorodiazirine (3) and the recently reported bis-(trifluoromethyl)diazirine (4), the diazirines which have been described in the literature have been substituted at the carbon atom by either hydrogen or hydrocarbon alkyl groups but not electron-withdrawing substituents. This paper describes the physical, spectral and some of the chemical properties of five previously undisclosed diazirines which are substituted by electron-withdrawing groups.

In general, the halo-diazirines which are described herein exhibit many of the spectral and chemical characteristics which have been previously described for difluorodiazirine (3). Thus, they are all colorless gases and are characterized by a family of 20-30 peaks in the 280-350 μ region in the ultraviolet spectra. In the infrared, the nitrogen-nitrogen double bond stretching vibration appears as an absorption of medium to medium-strong intensity at 6.25-6.50 microns. Although the thermal stability of the halo-diazirines reported in this paper is somewhat less than that of difluorodiazirine, they all undergo pyrolytic decomposition to the respective divalent carbon species and nitrogen.

Fluoromethoxydiazirine (II).

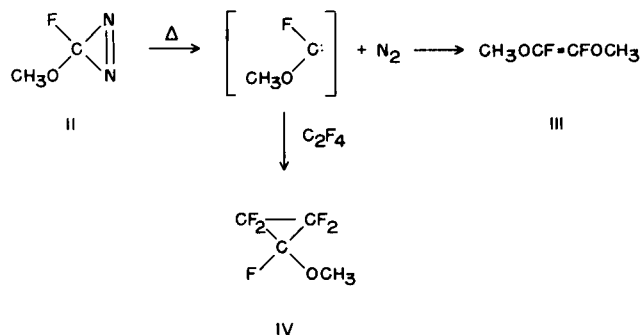
The identity of fluoromethoxydiazirine (II) was established on the basis of its elemental analyses



[*Anal.* calcd. for $C_2FH_3N_2O$: C, 26.7; F, 21.1; mol. wt., 90. Found: C, 26.6; F, 21.0; mol. wt., 93 (gas density method)], its spectral properties and

its chemical reactions. It is colorless, boils at about $5^\circ C.$, and exhibits single sharp peaks at $121.8\phi^*$ and 6.26τ in the F^{19} and H^1 n. m. r. spectra, respectively. The infrared spectrum shows an absorption of medium-strong intensity at 6.45 microns due to the nitrogen-nitrogen double bond. Other absorptions appear at 3.37 (w), 3.50 (w), 4.88 (w), 6.45 (ms), 6.84 (m), 7.73 (s), 8.22 (m), 8.58 (s), 9.80 (m) and 13.02 (w) microns. The mass spectral fragmentation pattern gives the following cationic species (relative abundance in parentheses): CH_2 , N (13.7), CH_3 (100.0), O, (1.8), N_2 , CO (23.2), CHO (21.2), CH_2O (3.6), CH_3O , CF (14.0), CHF (5.6), CH_3F (1.5), CH_2OC (5.6), CH_3OC (8.7), CFO (28.7), CN_2F (1.2) and CH_3OCF (3.1).

Chemically, fluoromethoxydiazirine (II) is more similar to difluorodiazirine (I) than to the hydrocarbon diazirines. However, in the presence of HF and H_2O , II appears to form CH_3OCF_2H which in turn is hydrolyzed to methyl formate. Thermal decomposition of II to fluoromethoxycarbene and nitrogen is readily accomplished by heating for 2 hours at steam bath temperature. In the absence of a co-reactant, the major product is 1,2-difluoro-1,2-dimethoxyethylene (III). However, in the presence of a five-fold excess of tetrafluoroethylene, methoxy-

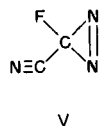


pentafluorocyclopropane (IV) is the product in a 61.5% yield. Lesser amounts of III are also formed. IV was identified by spectral comparisons with an au-

thetic sample which was prepared previously by the addition of difluorocarbene to trifluorovinylmethyl ether (5). Although fluoromethoxycarbene, CH_3OCF_2 , is thought to be an intermediate in certain hydrolysis reactions (6), this is the first demonstration of its existence by chemically trapping the species.

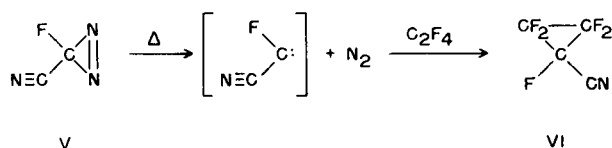
Cyanofluorodiazirine (V).

Cyanofluorodiazirine (b.p. -30°C .) is readily identified by the presence of the cyano absorption in the



infrared spectrum at 4.44 microns, the nitrogen-nitrogen double bond absorption at 6.34 microns and a single carbon-fluorine absorption at $157.8\mu^*$ in the n.m.r. spectrum. The mass spectrum and the elemental analyses are consistent with the assigned structure [*Anal.* Calcd. for C_2FN_3 : C, 28.2; F, 22.4; mol. wt., 85. Found: C, 28.1; F, 22.1; mol. wt., 86 (gas density method)].

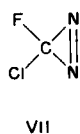
Thermal decomposition of cyanofluorodiazirine (V) is a source of the divalent carbon species, cyanofluorocarbene. Thus, cyanopentafluorocyclopropane



(VI) is obtained in a 60% yield when cyanofluorodiazirine is heated for $1\frac{1}{2}$ hours on a steam bath in the presence of excess tetrafluoroethylene. Cyclopropane VI was spectroscopically identical to an authentic sample of VI prepared by the addition of difluorocarbene to trifluoroacrylonitrile (5).

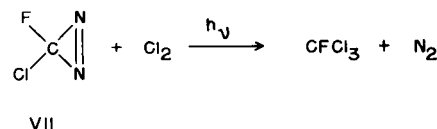
Chlorofluorodiazirine (VII).

Although elemental analyses were not obtained for chlorofluorodiazirine, spectroscopic and chemical evidence leave little doubt as to its structure. The infrared spectrum shows the expected nitrogen-



nitrogen stretching vibration as a medium absorption at 6.50 microns. Other absorptions appear at 8.23 (s), 8.32 (s), 9.45 (s), 11.02 (m) and 11.51 (w) microns. The ultraviolet spectrum shows the typical diazirine-type series of absorptions in the 280-350 $m\mu$ region (Figure 3). The mass spectral pattern shows the presence of both fluorine and chlorine bonded to carbon as well as fragments containing two nitrogen atoms. The normal isotopic distribution of chlorine³⁵ and chlorine³⁷ was observed (the chlorine³⁷ species are not reported here). The relative pattern percent is reported in parentheses following the cationic species; N (13.9), F (1.1), CN (6.3), N_2 (17.3), CF (100.0), NF (1.4), Cl^{35} (28.1), CNF (2.4), CCl^{35} (28.1), CF_2 (2.8), CN_2F (43.0), CNCl^{35} (3.0), CFCl^{35} (32.4), $\text{CN}_2\text{Cl}^{35}$ (9.9), CNFCl^{35} (0.5) and $\text{N}_2\text{FCl}^{35}$ (8.6).

In a manner analogous to experiments which have been reported previously for difluorodiazirine (3b), chlorofluorocarbene, generated by photolysis of VII at room temperature, reacts with chlorine to afford



a high yield of trichlorofluoromethane. Trace quantities of CCl_4 are also formed in the above photolysis.

Difluoramino-diazirines.

The two difluoramino-substituted diazirines which are reported here are being discussed together

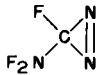
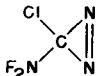


because of the obvious spectral and chemical similarities. Some of the physical and spectral properties of VIII and IX, as well as elemental analyses, are listed in Table I.

Like the other diazirines, VIII and IX are colorless gases which exhibit a family of peaks in the 280-340 $m\mu$ region in the ultraviolet spectra (see Figures 4 and 5). The infrared and mass spectra (Table II) are consistent with the assigned structures. The infrared absorptions for VIII are at 4.45 (w), 6.33 (m), 7.76 (s), 8.86 (m), 9.44 (w), 10.17 (s), 11.08 (s), and 12.03 (m) microns. Chlorodifluoramino-diazirine (IX) shows absorptions at 6.25 (m), 8.96 (ms), 9.40 (w), 10.47 (ms) and 11.06 (s) microns.

TABLE I

Properties of Difluoraminediazirines

Diazirine	Extrapolated b.p. (°C)	F ¹⁹ n.m.r. Spectrum φ*	Spectrum Group	Analyses		
				Calcd.	Found	
 (VIII)	-36	-38.7 +159.4	NF ₂ CF	C, F, N, m.w.,	10.8 51.4 37.8 111	11.3 51.9 38.8 111 (a)
 (IX)	+ 5	-50.2	NF ₂	C, N, m.w.,	9.4 32.9 127.4	9.5 32.5 129 (a), 128 (b)

(a) Gas-density method. (b) Effusion rate in mass spectrometer.

TABLE II

Mass Spectra (a)

m/e	Cationic Species	Relative Pattern Percent	
		NF ₂ CFN ₂ (VIII)	NF ₂ CClN ₂ (IX)
14	N	1.1	30.3
19	F		4.5
26	CN	4.0	29.1
28	N ₂	28.0	88.6
31	CF	100.0	30.4
33	NF	3.4	6.7
35	Cl ³⁵		74.5
40	CN ₂	0.7	13.0
45	CNF	22.2	26.1
47	CCl ³⁵		67.6
50	CF ₂	3.6	
52	NF ₂	3.3	6.3
59	CN ₂ F	8.8	
61	CNCl ³⁵		100.0
64	CNF ₂	27.7	17.8
66	CFCI ³⁵		5.2
69	CF ₃	1.4	
75	CN ₂ Cl ³⁵		17.3
80	CNFCI ³⁵		59.1
83	CNF ₃	5.1	
92	CN ₃ F ₂	2.4	19.2
99	CNF ₂ Cl ³⁵		4.6

(a) Normal isotopic distribution for Cl³⁵ and Cl³⁷ was observed. Cl³⁷ isomers are not reported.

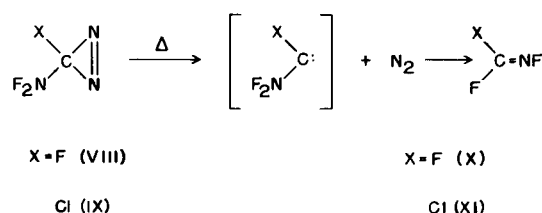
TABLE III

Ultraviolet Spectra

Diazirine	λ max (mμ)	ε (l mole ⁻¹ cm ⁻¹)
CH ₃ OCFN ₂ (II)	357.3	84.0
N≡CCFN ₂ (V)	337.9	153.0
ClCFN ₂ (VII)	351.3	184.5
NF ₂ CFN ₂ (VIII)	325.7	229.0
NF ₂ CClN ₂ (IX)	331.3	26.2

Unlike the other halo-diazirines (I, II, V and VII), VIII and IX are highly-explosive and are EXTREMELY sensitive to handling. It has been found that under no circumstances should vapor phase chromatography traps containing glass beads be used during separation procedures. Also, compound VIII should not be cooled to temperatures below -119°C . Diluents, such as CFCl_3 and CF_2Cl_2 , have been found to be effective in reducing the hazard of phase changes with VIII and IX.

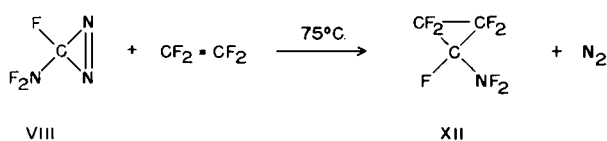
Chemically, difluoramino fluorodiazirine and chloro-difluoramino diazirine are quite interesting since the carbenes derived from these compounds exhibit both intra- and intermolecular reactions. Thus, thermal decomposition of pure difluoramino fluorodiazirine (VIII) at 75°C ., affords trifluoromethylenimine (X) as the major isolable product. In a similar manner, chlorodifluoramino diazirine (IX) at 50°C ., yields the *syn*- and *anti*-isomers of C-chlorodifluoromethylenimine (XI) resulting from a fluorine shift from the nitrogen to carbon. The identity of X and



XI was established by spectral comparisons with authentic samples (7).

In the presence of Lewis acids, such as boron trifluoride and aluminum chloride in Freon 113 solvent, decomposition of difluoramino fluorodiazirine occurs below room temperature. In the presence of BF_3 , trifluoromethylenimine (X) is the major product. On the other hand, with AlCl_3 , the isomers of C-chlorodifluoromethylenimine (XI) are obtained. It is interesting to note that the ratio of *syn*- to *anti*-isomers (fluorine atoms) obtained in the AlCl_3 decomposition was consistently about 3.7 to 1.0 and is quite similar to the ratio obtained in the photo-chlorination of C-bromodifluoromethylenimine (7).

The generation of difluoramino fluorocarbene, $\text{NF}_2\text{CF:}$, from difluoramino diazirine was demonstrated in a more classical manner by trapping the reactive intermediate with an olefin. Thus, in the presence of a five-fold excess of tetrafluoroethylene, difluoramino pentafluorocyclopropane (XII) was obtained in a 36.8% yield. The identity of XII was



established on the basis of elemental [*Anal.* Calcd. for $\text{C}_3\text{F}_7\text{N}$: C, 19.7; F, 72.7; mol. wt., 183. Found: C, 19.4; F, 72.7; mol. wt., 181 (gas density method)] and spectral analyses. The mass and infrared spectra are consistent with the assigned structure. The F^{19} n.m.r. spectrum shows a broad absorption at $-34.3\phi^*$ (NF_2), an AB pattern at 151.6 and $152.2\phi^*$ (CF_2) and a single peak at $204.9\phi^*$ (CF) in the area ratio of 2:4:1.

Ultraviolet Spectra.

Although no detailed interpretation and discussion of the ultraviolet spectra of the halo-diazirines described in this paper will be attempted, the spectra are presented because of the obvious similarities between compounds. All of the spectra (Figures 1-5) exhibit vibrational fine structure; however, the spectra of the diazirines with relatively large groups attached to the ring (II, VIII and IX) are broadened considerably.

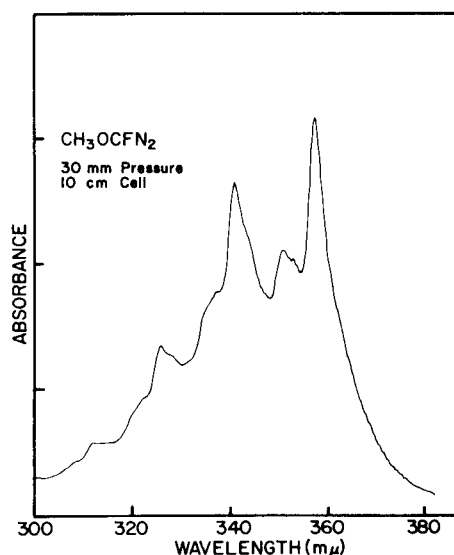


Fig. 1. Ultraviolet Spectrum of CH_3OCFN_2

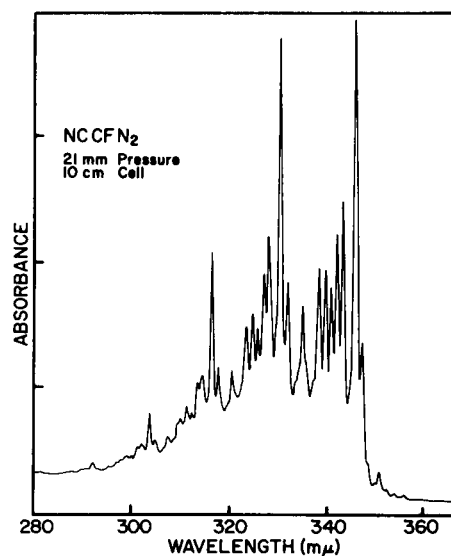
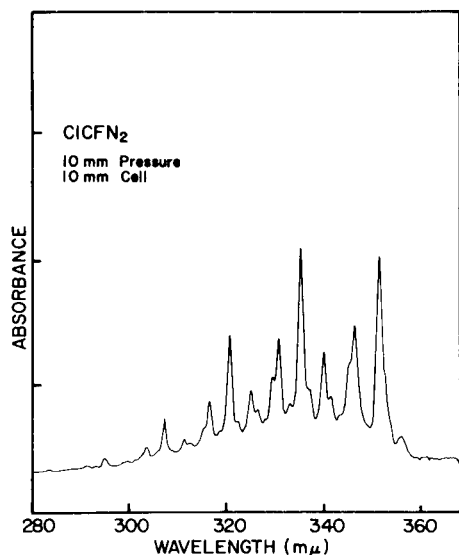
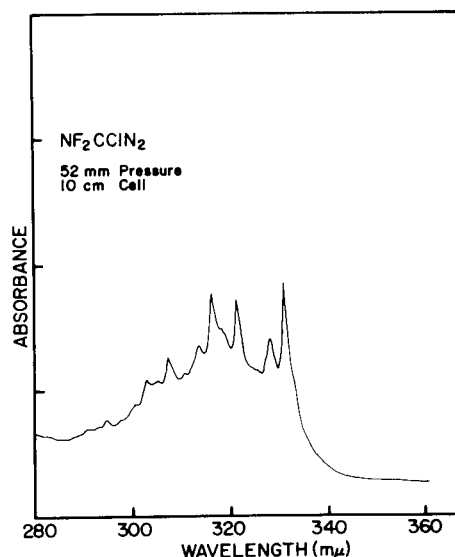
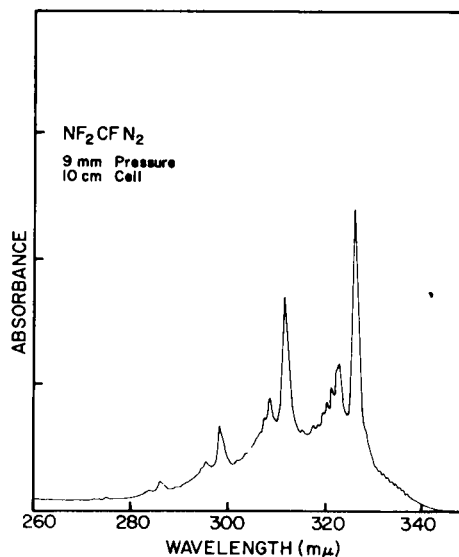


Fig. 2. Ultraviolet Spectrum of NCCFN_2

Fig. 3. Ultraviolet Spectrum of ClCFN₂Fig. 5. Ultraviolet Spectrum of NF₂CCIN₂Fig. 4. Ultraviolet Spectrum of NF₂CFN₂

EXPERIMENTAL

General.

Infrared spectra were obtained on a Perkin-Elmer Model 21 double beam instrument using a 2.5-cm. gas cell with NaCl windows. Fluorine and proton nuclear magnetic resonance spectra were measured with a Varian V-4300-2 instrument operating at 40.0 mc.; internal standards of CFCl₃ and (CH₃)₄Si were used for the determination of shielding values. The shielding values are reported in phi (8) and tau (9) units for fluorine and proton, respectively, at dilutions of 20-30% by volume. The mass spectra were obtained on a Consolidated 21-103C instrument at an ion chamber temperature of 250°C., with an ion voltage of 70 and an ion current of 10 μA. Ultraviolet spectra were measured on a Cary Model 11 Recording Spectrometer using 10-cm. gas cells.

Pyrolysis of Diazirines.

A 1-2 millimole sample of pure halo-diazirine was condensed into a 20-ml. heavy-wall glass ampoule and the ampoule sealed. The

ampoule was then slowly heated to and maintained at 50-95°C., for 1-18 hours. At the end of the reaction time, the ampoule was cooled to -196°C., opened and the contents separated by fractional distillation-condensation techniques using appropriately cooled traps. Preparative vapor phase chromatography was utilized to isolate the pure components. The yields mentioned in the discussion represent the quantity of pure product which was obtained by chromatographic trapping techniques.

Synthesis of Cyclopropanes.

A mixture of 1 millimole of halo-diazirine and 5-10 millimoles of tetrafluoroethylene was condensed into a 20-ml. heavy-wall glass ampoule and the ampoule sealed. The mixture was heated to 50-95°C., for 1-18 hours and then separated as outlined above.

Acknowledgments.

The authors wish to express their appreciation to Mr. A. H. Stoskopf, Mr. W. H. Swanson and Mr. D. P. Babb for excellent technical assistance, Dr. J. J. McBrady for infrared and nuclear magnetic resonance measurements and interpretation and Mr. P. B. Olson for analytical determinations.

This work was supported in part by the Advanced Research Projects Agency under Contract NOrd 18688, and was monitored by the Bureau of Naval Weapons.

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Received August 16, 1965

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