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Pyrolysis of Fluorodiazirines

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The thermal decomposition of difluorodiazirine and difluoramino fluorodiazirine results in the formation of difluorocarbene and difluoramino fluorocarbene, respectively. The isolable products of the pyrolyses include fluoro-alkenes, -cyclopropanes, -azines, -aziridines and in some cases isomerization products thereof.

Introduction.

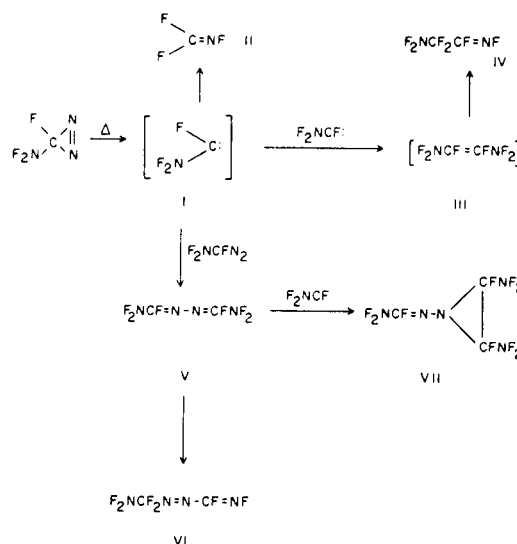
Previous publications dealing with the pyrolysis of halodiazirines have described the generation of halocarbenes and the resultant formation of alkenes, cyclopropanes and azines (1). In addition, pyrolysis of chlorodifluoramino diazirine and difluoramino fluorodiazirine was reported to yield fluoromethylenimine derivatives resulting from intramolecular fluorine migration in the initially formed carbenes (1b). It is the object of this paper to describe a number of intermolecular carbene reaction products isolable from the pyrolysis of difluorodiazirine and difluoramino fluorodiazirine.

Results and Discussion.

Pyrolysis of difluorodiazirine, CF_2N_2 , was carried out under autogeneous pressure at 125° ($t_{1/2} \sim 6$ hours at 125°) in a stainless steel autoclave whereas pyrolysis of difluoramino fluorodiazirine, NF_2CFN_2 , diluted with dichlorodifluoromethane, CF_2Cl_2 (2), was conveniently accomplished by heating in glass ampoules at $75\text{--}80^\circ$ for a period of 18-24 hours. In both cases, the nature of all products isolated can be rationalized on the basis of reactions involving carbene intermediates. However, the reaction mixture obtained from the pyrolysis of difluoramino fluorodiazirine was more complicated because of the possibility of intramolecular isomerization products resulting from fluoride shifts from nitrogen to carbon.

Thus, the major pyrolysis products are perfluoromethylenimine, $\text{CF}_2=\text{NF}$, from difluoramino fluorodiazirine, NF_2CFN_2 , and perfluorocyclopropane, $\text{CF}_2\text{CF}_2\text{CF}_2$, from difluorodiazirine, CF_2N_2 . Perfluorocyclopropane undoubtedly results from the further addition of difluorocarbene to tetrafluoroethylene, which is the usual difluorocarbene-dimerization product. Under the pyrolysis conditions in which difluorodiazirine was undergoing slow decomposition, tetrafluoroethylene is an efficient scavenger for difluorocarbene and thus was not detected in the products.

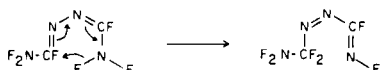
During the pyrolysis of difluoramino fluorodiazirine, dimerization of difluoramino fluorocarbene, I, undoubtedly leads to 1,2-bis(difluoramino)-1,2-difluoroethylene, III, however, under the reaction conditions this α,β -unsaturated difluoramino derivative undergoes a facile isomerization to the fluorimine IV. In this manner, the ethylene derivative is removed from further reaction with the carbene and no cyclopropane formation is observed. Perfluoro-1,4-diazabut-1-ene, IV, which was isolated in a 16% molar yield was identified by infrared, F^{19} nuclear magnetic resonance and mass spectroscopy.



The infrared spectrum of IV shows strong NF absorption in the $10.4\text{--}10.8\ \mu$ region as well as the fluorimine unsaturation at $5.94\ \mu$. The F^{19} n.m.r. spectrum exhibits the following peaks in the expected area ratios: $-20.8\phi^*$ (NF_2), $11.2\phi^*$ ($=\text{NF}$), $75.3\phi^*$ (CF, doublet, $J = 30$ cps) and $106.6\phi^*$ (CF_2). The mass spectrum is also consistent with the proposed structure.

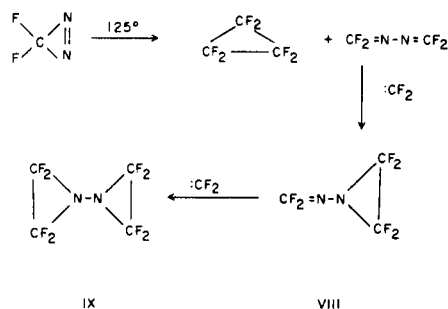
The formation of the difluoramino-substituted azine, V, by the reaction of difluoramino fluorocarbene with the parent diazirine, NF_2CFN_2 , (or its thermally isomerized acyclic form) is analogous with that which has been reported for difluorodiazirine, (1a), chloromethoxydiazirine (1c) and chlorophenyldiazirine (1c).

The isomers, V and VI, were isolated in a combined molar yield of about 10% with the ratio of V and VI usually about 1 to 4. The difluoramino-substituted azine, V, isomerizes readily to the azo-fluorimine, VI, in the presence of fluoride ion and, like IV, illustrates the facile isomerization of α,β -unsaturated difluoramino compounds. In this case, the isomerization involves an overall 1,5-fluoride shift perhaps involving a cyclic transition state as shown below.



Although difficult to separate by vapor phase chromatography, the isomers, V and VI, are clearly distinguishable by infrared and F^{19} nuclear magnetic resonance spectroscopy. The infrared spectrum of perfluoro-1,3,4,6-tetraza-hexa-2,4-diene, V, shows an absorption due to the $>\text{C}=\text{N}$ - groups at $5.80\ \mu$, whereas that of perfluoro-1,3,4,6-tetraza-hexa-1,3-diene, VI, exhibits absorptions at $6.00\ \mu$ and $6.53\ \mu$ due to the $>\text{C}=\text{NF}$ and azo group, respectively. The F^{19} n.m.r. spectra of the isomers are also consistent with the proposed structures. Compound V shows only two F^{19} n.m.r. peaks in the area ratio of about 2:1. The absorption for the $-\text{NF}_2$ is at $-42.8\phi^*$ and that for the CF peak appears as a triplet ($J = 21$ cps) at $65.5\phi^*$. On the other hand, the F^{19} n.m.r. spectrum of the azo-fluorimine isomer, VI, shows peaks at $-19.0\phi^*$ ($-\text{NF}_2$), $-7.7\phi^*$ ($=\text{NF}$), $80.2\phi^*$ (CF, doublet, $J = 5.9$ cps) and $102.6\phi^*$ (CF_2) in the expected area ratios.

Although halo-carbenes have been reported to add to carbon-nitrogen double bonds, the further addition of the respective fluorocarbene to the azomethine group in V, to form the fluoroaziridine, VII, is without precedent in fluorocarbene chemistry and represents a low yield route to a new class of compounds. Further members of this class of compounds were obtained from the pyrolysis of difluorodiazirine also, as shown below:



The identity of *N*-(2,2,3,3-tetrafluoroaziridyl)difluoromethylenimine, VIII, was established by elemental analysis, infrared, F^{19} n.m.r. and mass spectroscopy and pyrolysis studies. Its infrared spectrum shows the presence of the $>\text{C}=\text{N}$ - group at $5.68\ \mu$ and the perfluoroaziridyl ring at $6.60\ \mu$ (4), and its F^{19} n.m.r. spectrum exhibits a somewhat broadened absorption at $126.3\phi^*$ (ring CF_2) and a typical $\text{CF}_2=\text{N}$ - AB pattern at 49.4 and $75.7\phi^*$ ($J_{\text{AB}} = 65.2$ cps). The mass spectrum is consistent for the structure assigned and shows a parent peak 178 (6%) $\text{C}_3\text{F}_6\text{N}_2$.

Utilizing the spectroscopic properties of VIII as a reference, the identity of *N*-2,3-bis(difluoramino)-2,3-difluoro-1-aziridyl difluoramino fluoromethylenimine, VII, obtained in a molar yield of about 2% from the pyrolysis of NF_2CFN_2 , was established primarily on the basis of spectral considerations and its molecular weight.

The infrared spectrum of VII shows the presence of the $\text{C}=\text{N}$ - group at $5.82\ \mu$ (compare with $\text{NF}_2\text{CF}=\text{N}=\text{CFNF}_2$ and $\text{C}_2\text{F}_5\text{N}=\text{CFCF}_3$ which absorb at $5.80\ \mu$) as well as complex NF absorptions in the 10.4 - $11.4\ \mu$ region. However, of primary importance is an absorption of strong intensity of $6.90\ \mu$. The 6.6 - $7.0\ \mu$ region has been shown to be particularly diagnostic for the presence of three-membered ring fluorinated heterocycles of oxygen, sulfur and nitrogen containing one heteroatom (4).

TABLE I

Vapor Phase Chromatography Results

Compound	T_{r} (a)
F_2NCFN_2	50 (c)
$\text{CF}_2=\text{NF}$ (II)	48 (b)
$\text{F}_2\text{NCF}_2\text{CF}=\text{NF}$ (IV)	150 (c)
$\text{F}_2\text{NCF}_2\text{N}=\text{NCF}=\text{NF}$ (VI)	246
$\text{F}_2\text{NCF}=\text{N}=\text{N}=\text{CFNF}_2$ (V)	278
$\text{F}_2\text{NCFCF}(\text{NF}_2)\text{N}=\text{N}=\text{CFNF}_2$ (VII)	847
CF_2N_2	11 (c)
$\text{CF}_2\text{CF}_2\text{CF}_2$	45 (c)
$\text{CF}_2=\text{N}=\text{N}=\text{CF}_2$	38
$\text{CF}_2=\text{N}=\text{N}=\text{CF}_2\text{CF}_2$ (VIII)	47
$\text{CF}_2\text{CF}_2\text{N}=\text{NCF}_2\text{CF}_2$ (IX)	68

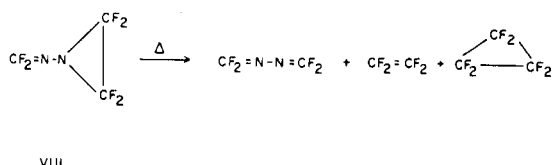
(a) $T_{\text{r}} = \text{Relative retention time} = \frac{T_{\text{cpd}} \cdot T_{\text{air}}}{T_{\text{Ref}} \cdot T_{\text{air}}} \times 100$. T_{r} relative to CFCl_3 unless otherwise stated. (b) 2m. x $\frac{1}{2}$ " 33% FC-43 (perfluorotributylamine) on Celite operating at -25°C . T_{r} relative to CF_2Cl_2 . (c) T_{r} relative to CF_2Cl_2 .

The molecular weight of VII was found to be 275 (effusion rate in mass spectrometer) compared with a calculated value of 277. The mass spectrum provided additional confirmatory evidence, including a small parent peak corresponding to $C_3F_9N_5$.

As shown in the reaction scheme above, difluorocarbene not only reacts with tetrafluoro-2,3-diazabuta-1,3-diene to form VIII but also adds to the azomethine group of VIII to form the bisaziridine, IX. At 125° the yield of IX was 0.01%. Identification was by molecular weight, infrared, F^{19} n.m.r. and mass spectroscopy.

The infrared spectrum of IX shows a principal absorption due to the three-membered ring at 6.63μ . The F^{19} n.m.r. spectrum shows a single peak at $125.4\phi^*$ corresponding to the CF_2 groups and the molecular weight by effusion in the mass spectrometer was found to be 221 ± 5 (theory = 228). The mass spectrum is consistent with the assigned structure.

In seeking an explanation for the extremely low yields of the perfluoroaziridyl compounds, the thermal decomposition of $CF_2=N-N=CF_2$ in a Monel cylinder was examined quantitatively at 134.6° and an initial pressure of 150 mm. The primary decomposition, yielding difluorocarbene and $CF_2=N-N=CF_2$, appears to be unimolecular. The half-life of VIII at 134.6° is 5.6 hours in the reaction



leading to $CF_2=N-N=CF_2$, C_2F_4 and $c-C_3F_6$. Thus, the rate of thermal decomposition of VIII ($t_{1/2} = 5.6$ hour at 134.6°) is comparable with that of difluorodiazirine and accounts for the low yields of the three-membered ring products.

EXPERIMENTAL

General.

Infrared spectra were obtained on a Perkin-Elmer Model 21 double beam instrument using a 2.5-cm. gas cell with sodium chloride windows. Fluorine nuclear magnetic resonance spectra were measured with a Varian V-4300-2 instrument operating at 40.0 mc.; an internal standard of trichlorofluoromethane was used for the determination of shielding value. The shielding values are reported in phi (ϕ^*) (5) units, at dilutions of 20-30% by volume. Chromatographic separations were performed at 25° with a Model 154-D Perkin-Elmer Vapor Fractometer, utilizing a $\frac{1}{2}$ " O.D. tube two meters long and packed with 33% KF-8126 oil on Celite. The relative retention times of the pyrolysis products are shown in Table I. The mass spectra were obtained on a Consolidated 21-103C instrument at an ion chamber temperature of 250° with an ion

voltage of 70 and an ion current of 10 μ A, and are expressed as m/e (relative intensity) assigned ion.

Pyrolysis of Difluorodiazirine.

A 26.0 g. (0.333 mole) sample of difluorodiazirine was pressurized into a 350 ml. Monel autoclave and heated to 125° for 24 hours. After the pyrolysis period, the volatile contents of the autoclave were transferred into a vacuum system and separated by fractional distillation-condensation employing traps cooled to -78° and -196° . Final purification was accomplished by vapor phase chromatography (see Table I).

Perfluorocyclopropane (12.6 g., 75%) and $CF_2=N-N=CF_2$ (4.5 g., 21%) were identified by spectral comparisons with authentic samples. The aziridine VIII, $CF_2=N-N=CF_2$ (0.7 g., 4%), showed the following mass spectral fragmentation pattern: 14(1.3)N, 26(1.2)CN, 28(2.8)N₂, 31(60.8)CF, 45(2.9)CFN, 50(100)CF₂, 64(1.4)CF₂N, 69(33.3)CF₃, 78(4.9)CF₂N₂, 81(8.2)C₂F₃, 100(37.9)C₂F₄, 109(18.1)C₂F₃N₂, 114(9.1)C₂F₄N, 128(9.3)C₂F₄N₂ and 178(6.0)C₃F₆N₂.

Anal. Calcd. for $C_3F_6N_2$: F, 64.0; N, 15.7. Found: F, 63.2; N, 16.0.

The bisaziridine, IX, $CF_2CF_2N-N=CF_2$, was obtained in only 0.01% yield (0.02 g.) and was identified on the basis of spectral considerations and molecular weight. The mass spectrum showed the following pattern: 14(2.7)N, 19(1.1)F, 26(1.6)CN, 28(4.9)N₂, 31(100)CF, 38(1.5)C₂N, 40(6.9)CN₂, 43(1.0)C₂F, 45(3.3)CNF, 50(83.1)CF₂, 64(3.6)CF₂N, 69(88.3)CF₃, 79(1.4)C₂F₂N, 78(1.1)CF₂N₂, 81(37.3)C₂F₃, 95(1.2)C₂F₃N, 100(98.2)C₂F₄, 109(15.2)C₂F₃N₂, 114(4.8)C₂F₄N, 128(6.0)C₂F₄N₂, and 159(1.6)C₃F₅N₂.

Pyrolysis of Difluoroaminofluorodiazirine.

In three experiments, a total quantity of difluoroaminofluorodiazirine amounting to 0.826 g. (7.44×10^{-3} mole), diluted with 0.291 g. (2.4×10^{-3} mole) of dichlorodifluoromethane, was condensed into 2 ml. glass ampoules cooled to -196° and fitted with Fischer-Porter Teflon valves. The ampoules were allowed to warm slowly to room temperature and then heated to and maintained at $75-80^\circ$ for 24 hours. After the pyrolysis was complete, the contents of the ampoules were combined and separated by fractional distillation-condensation on a vacuum line employing traps cooled to -78° , -111° , -145° and -196° . The reaction mixture was found to have the following product distribution (in molar percent yield (6)): -78° (17-19%), -111° (19-21%), -145° (CF_2Cl_2) and -196° (41-47%). Final purification was accomplished by vapor phase chromatography using a Kel-F 8126 (33% on Celite) column. The relative retention times of the purified products are shown in Table I. The mass spectral pattern of VII is summarized below:

14(5.4)N, 28(9.5)N₂, 31(100)CF, 33(10.2)FN, 45(18.3)CFN, 50(15.6)CF₂, 52(17.1)F₂N, 64(75.6)CF₂N, 69(29.5)CF₃, 76(12.4)C₂F₂N, 81(5.6)C₂F₃, 83(13.2)CF₃N, 90(5.4)C₂F₂N₂, 95(5.8)C₂F₃N, 109(17.5)C₂F₃N₂, 135(10.4)C₃F₃N₃, 142(6.6)C₂F₄N₃, 147(5.2)C₂F₅N₂ and 225(5.1)C₃F₇N₄.

Pyrolysis of $CF_2=N-N=CF_2$

The pyrolysis of $CF_2=N-N=CF_2$ was conducted in 90 ml. Monel cylinder heated at 134.6° according to the procedure described previously for perfluorovinyl- and perfluoroallylcyclopropane (7).

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