Reactions of Pentafluoroguanidine and Tetrafluoroformamidine with Alkali Metal Fluorides. Fluorine-Containing Diaziridines

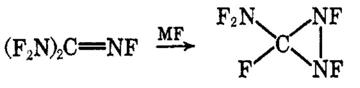
WILLIAM C. FIRTH, JR.

American Cyanamid Company,[1] Stamford Research Laboratories,
Stamford, Connecticut 06904

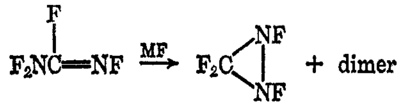
Received March 27, 1968

3-Difluoramino-1,2,3-trifluorodiaziridine (1) and tetrafluorodiaziridine (2) were prepared by the reactions of pentafluoroguanidine and tetrafluoroformamidine, respectively, with alkali metal fluorides. Tetrafluoroformamidine was also dimerized by alkali metal fluorides.

Two members of a new class of diaziridines,[2] have been prepared by a novel rearrangement reaction which pentafluoroguanidine[3] and tetrafluoroformamidine[3b] undergo in the presence of certain alkali metal fluorides.[4] Dimerization of tetrafluoroformamidine was competitive with formation of the diaziridine (2).



1 (1)



2 (2)

The reactions were usually carried out by condensing either pentafluoroguanidine or tetrafluoroformamidine into an evacuated Pyrex glass reactor containing the alkali metal fluoride. The reactor was then allowed to warm to room temperature. Both liquid–solid and gas–solid reactions could have occurred under these conditions. After the desired time at room temperature, the products were separated by fractionation in a vacuum line and/or fractional codistillation.[5]

Diaziridines 1 and 2 were volatile compounds and, at room temperature, were ordinarily kept in the gas phase at low pressures. Since they appeared to be unstable at room temperature in Pyrex glass, they were stored at −78°. Numerous explosions occurred when 1 or 2 were condensed or volatilized. (See the Experimental Section for more details.) The dimer of tetrafluoroformamidine appeared to be more stable than 1 and 2 and could be stored at room temperature.

The rearrangement and dimerization of tetrafluoroformamidine can be controlled to give either the diaziridine (2) or dimer as the principal product. For example, a reaction of tetrafluoroformamidine with potassium fluoride in the presence of a diluent gave largely diaziridine, while a reaction with cesium fluoride gave essentially complete conversion into the dimer. Rubidium fluoride gave an intermediate mixture of diaziridine and dimer. The dimer content increased when the rubidium fluoride/tetrafluoroformamidine ratio was increased or the reactor volume was decreased.

The alkali metal fluorides would be expected to show an order of reactivity in which CsF > RbF > KF.[6] This would account for the dependence of product composition on alkali metal fluoride. However, other factors, *e.g.*, particle size of the alkali metal fluoride, could also affect the reactivities of the alkali metal fluoride and were not controlled in these experiments.

3-Difluoramino-1,2,3-trifluorodiaziridine (1).—Usually rubidium fluoride was used to convert pentafluoroguanidine into the diaziridine. A mixture of pentafluoroguanidine and cesium fluoride exploded when allowed to warm spontaneously toward room temperature. However, a controlled reaction took place when the same reagents were allowed to warm slowly over a period of several hours from −132 to −30°. Potassium fluoride converted gaseous pentafluoroguanidine into the diaziridine.

Carbon tetrafluoride, silicon tetrafluoride, both isomers of difluorodiazine,[7] carbon dioxide, and other impurities were also observed in the reaction products. The yield of purified diaziridine (1) from one run was 25%.

The structure of 1 is based on the following evidence. Fractional codistillation indicated that 1 was similar, but lower, in boiling point compared to pentafluoroguanidine. Molecular weight data (found, 146, gas density; calcd, 149) also indicated isomerization. Fluorine nmr analysis[8–10] showed peaks at ϕ^* 159.2 (one F, slightly broadened, C–F), −30.4 (two F, broad, NF_2), 24.1 (one F, broad, N–F), and 32.7 (one F, broad, N–F). This data strongly indicates the diaziridine structure 1. The N–F groups in the ring give rise to two peaks either because of a *trans* ori-

---

[1] This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by the Bureau of Naval Weapons, RMMP, under Contract No. NOrd 18728.

[2] The preparation and chemistry of diaziridines have been reviewed by E. Schmitz, *Angew. Chem. Intern. Ed. Engl.*, **3**, 333 (1964). See also E. Schmitz, "Organische Chemie in Einzeldarstellwunge," Bd. IX, Springer-Verlag, Berlin, 1967; *Chem. Abstr.*, **67**, 116883 (1967).

[3] (a) R. A. Davis, J. L. Kroon, and D. A. Rausch, *J. Org. Chem.*, **32**, 1662 (1967); (b) R. J. Koshar, D. R. Husted, and C. D. Wright, *ibid.*, **32**, 3859 (1967).

[4] W. C. Firth, Jr., U. S. Patent 3,345,359 (1967) and U. S. Patent 3,345,360 (1967).

[5] G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

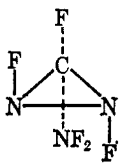
[6] T. A. Gens, J. A. Wethington, Jr., A. R. Brosi, and E. R. Van Artsdalen, *J. Amer. Chem. Soc.*, **79**, 1001 (1957); see also R. Stephens and J. C. Tatlow, *Quart. Rev.* (London), **16**, 44 (1962).

[7] C. B. Colburn, F. A. Johnson, A. Kennedy, K. McCallum, L. C. Metzger, and C. O. Parker, *J. Amer. Chem. Soc.*, **81**, 6397 (1959). See also C. B. Colburn in "Advances in Fluorine Chemistry," Vol. 3, M. Stacey, J. C. Tatlow, and A. G. Sharpe, Ed., Butterworth, Inc., Washington, D. C., 1963, p 113.

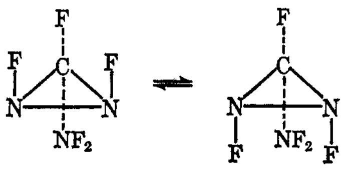
[8] The spectrum of a solution of the compound in trichlorofluoromethane was obtained with a Varian DP-60 high resolution spectrometer operating at 56.4 Mc. Chemical shifts are expressed in terms of ϕ^* values (parts per million): G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

[9] In addition to the peaks for 1, very weak peaks assignable to tris(difluoramino)fluoromethane[10] at ϕ^* 138.2 and −23.2 were observed.

[10] The reported[3b] values are ϕ^* 138.7 and −23.2.



1a



1b

entation to one another (**1a**) or slow inversion (**1b**).[11] Rapid inversion would average the environments of the two NF groups and result in a single absorption peak. The infrared spectrum showed a strong CF band at 7.26 μ and strong absorptions in the NF region. The CF absorption is at an abnormally low wavelength compared to other compounds containing CF and NF_2 groups, but is similar to the CF bands of the product from the analogous reaction of tetrafluoroformamidine. Another band at 7.91 μ in the infrared spectrum of **1** varied somewhat in intensity from sample to sample, but was never completely missing. It may be caused, at least in part, by tris(difluoramino)fluoromethane (also detected in the fluorine nmr spectrum).[9,10] Finally, the mass spectrum of **1**, shown in Table I, is consistent with the proposed structure. Typically for a difluoramino compound, the largest fragment is equivalent to the loss of NF_2 from the parent molecule. The abundant CF fragment is in agreement with the infrared and nmr spectra. The spectrum shows an abundant N_2^+ fragment, which is not observed in the spectra of tetrafluorodiaziridine (**2**) (Table II) and the dimer of tetrafluoroformamidine (Table III). This fragment may be characteristic of a 3-difluoramino-1,2-difluorodiaziridine,  $F_2N\overline{\underset{|}{C}NFN}F$, since the two other compounds do not contain this type of grouping.

TABLE I

MASS SPECTRUM OF 3-DIFLUORAMINO-1,2,3-TRIFLUORODIAZIRIDINE[a,b]

m/e	Pattern	Indicated positive ion
97	0.11	CF_3N_2
83	0.45	CF_3N
69	0.25	CF_3
64	0.91	CF_2N
52	0.13	F_2N
50	0.21	CF_2
45	0.20	CFN
33	0.26	FN
31	1.00	CF
28	0.69	N_2
20	0.19	HF
19	0.06	F

[a] The spectrum was obtained on a Model 21-103 CEC mass spectrometer: ionizing current, 95 μA; ionizing voltage, 70 V; inlet, room temperature; ionization chamber, 270°.

Tetrafluorodiaziridine (**2**).—This compound was obtained by the reaction of tetrafluoroformamidine with either potassium fluoride or rubidium fluoride. The diaziridine **2** appeared to be even less stable than **1** and frequently exploded. Structure **2** is based on the following evidence. Fractional codistillation indicated that the compound was similar, but lower, in boiling point compared to tetrafluoroformamidine. Molecular weight data on the product of the reaction of tetrafluoroformamidine with potassium fluoride in the presence of bis(difluoramino)difluoromethane indicated that **2** was a rearrangement product. Infrared and fluorine nmr data showed the expected similarities to the corresponding spectra of **1**. However, **2** possesses a CF_2 group as shown by the presence of the symmetric and asymmetric CF_2 vibrations at 7.09 and 7.37 μ. Again the wavelength of the CF absorptions were unusually low. Fluorine nmr analysis[8] showed strong peaks at ϕ^* 119.9 (two F, sharp, CF_2) and 32 (two F, broad, -NF-NF-).[12] The mass spectrum of **2** (Table II) does not show the parent peak. Apparently the largest fragment results from loss of NF.

TABLE II

MASS SPECTRUM OF TETRAFLUORODIAZIRIDINE[a,b]

m/e	Pattern	Indicated positive ion
83	0.18	CF_3N
69	0.27	CF_3
64	0.17	CF_2N
52	0.03	F_2N
50	1.00	CF_2
45	0.06	CFN
33	0.11	FN
31	0.34	CF
20	0.03	HF
19	0.03	F

[a] See footnote *a* in Table I for conditions. [b] An effusion study indicated that all of the ions except possible F_2N^+ came from one compound.

TABLE III

MASS SPECTRUM OF THE DIMER OF TETRAFLUOROFORMAMIDINE[a]

m/e	Pattern	Indicated positive ion
128	1.000	$C_2F_4N_2$
114	0.066	C_2F_4N
109	0.384	$C_2F_3N_2$
102	0.656	CF_4N
95	0.323	C_2F_3N
83	0.446	CF_3N
69	1.962	CF_3
64	0.543	CF_2N
59	0.163	CFN_2
52	0.146	F_2N
50	0.570	CF_2
45	0.201	CFN
33	0.270	FN
31	0.962	CF
26	0.061	CN
20	0.178	HF
19	0.049	F

[a] An effusion study indicated that this sample was of high purity.

The reaction of **2** with ferrocene to form difluorodiazirine[13] is additional, although not conclusive, evidence for the diaziridine structure. According to an

---

[11] A number of reports have indicated that nitrogen atoms in a number of compounds related to this diaziridine have considerable configurational stability: W. D. Emmons, *J. Amer. Chem. Soc.*, **79**, 5739 (1957); F. A. Johnson, C. Haney, and T. E. Stevens, *J. Org. Chem.*, **32**, 466 (1967); A. Mannschreck, R. Radeglia, E. Grundemann, and R. Ohme, *Ber.*, **100**, 1778 (1967); S. J. Brois, *J. Amer. Chem. Soc.*, **90**, 506, 508, 1680 (1968).

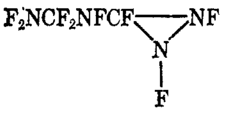
[12] In addition to these strong peaks, very weak, sharp absorptions were also observed at ϕ^* 63.4, 72.6, and 83.4.

[13] R. A. Mitsch, *J. Heterocycl. Chem.*, **3**, 245 (1966).

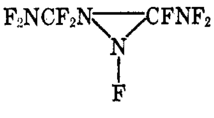
infrared spectrum, no reaction took place between 2 and air during several hours at room temperature.

The Dimer of Tetrafluoroformamidine.—As mentioned above, dimerization of tetrafluoroformamidine competes with the rearrangement reaction. The dimer of tetrafluoroformamidine was formed to some extent in all of the reactions of tetrafluoroformamidine with alkali metal fluorides. In the case of cesium fluoride, essentially complete dimerization rapidly occurred, as shown by a pressure drop to one-half the original value. Infrared and nmr spectra, mass spectrometry, and molecular weight data were used to characterize the dimer.

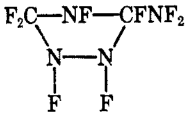
The infrared spectrum shows a CF absorption at 7.1 μ, the low wavelength region characteristic of **1** and **2**. Additional CF absorptions at higher wavelengths as well as strong absorptions in the NF region are also present. The fluorine nmr spectrum obtained at room temperature[14] showed absorptions assigned to CF (ϕ^* 150.4, doublet with $J \sim 18$ cps, 1 F), CF_2 (ϕ^* 92.9, center peak of a partially resolved AB pattern, 2 F), NF (ϕ^* 10.5, broad, 1 F), and NF_2 (ϕ^* −21.1, broad, 2 F) groups. Two additional peaks at ϕ^* −36.0 (broad, 1 F) and −33.3 (broad, 1 F) were also present. The latter two peaks could conceivably be either the center two peaks of the AB pattern of an NF_2 group attached to an asymmetric carbon atom, or two NF groups. Thus the structures **3a**, **3b**, and **3c** appear to fit this nmr data fairly well. However, the



3a



3b



3c

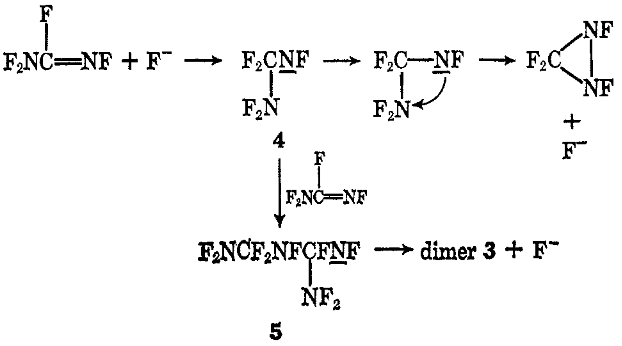
peaks at ϕ^* −36 and −33 are in the chemical-shift region for an NF_2 group and are considerably lower than the positions of the diaziridine NF groups found for **1** and **2**. Thus the fluorine nmr spectrum tends to favor **3b**. Another piece of evidence is the mass spectrum (Table III). The largest mass is equivalent to the parent peak minus two NF_2 fragments. This, of course, is much easier to rationalize in terms of **3b** rather than **3a** or **3c**, especially since tetrafluorodiaziridine lost NF rather than NF_2 from the parent molecule. Therefore, the nmr data and mass spectrum strongly favor structure **3b**.

Possible Mechanisms.—Pentafluoroguanidine and tetrafluoroformamidine are similar to certain other highly fluorinated, unsaturated compounds in their susceptibility to attack by alkali metal fluorides.[15] Such attack can cause rearrangement[16] as well as dimerization[17] and other reactions.

A possible mechanism for the formation of the diaziridines is given in Scheme I.

In this mechanism an attack on the electrophilic carbon–nitrogen double bond by a nucleophilic fluoride ion results in the formation of a fluoramide anion. Displacement of a fluoride ion from the geminal NF_2 group forms the diaziridine ring. Instead of cyclizing, the fluoramide anion might attack the carbon–nitrogen double bond of tetrafluoroformamidine to form **5**, which then gives dimer **3** by loss of fluoride ion.

SCHEME I



Other mechanisms involving the loss of fluoride ion from **4**, followed by intramolecular insertion of the electron-deficient nitrogen atom into an N–F bond of the difluoramino group or intermolecular addition to a fluorimino group can be written. Studies have indicated that diaziridine rings in other systems were formed by an intramolecular nucleophilic displacement rather than addition of electron-deficient nitrogen to a double bond.[2] The fluorimino–alkali metal fluoride system, however, is significantly different from those on which the mechanistic studies were made, because of possible effects caused by the surface of the metal fluoride and the effects of fluorine substitution on reactivity of the intermediates.

Experimental Section

Caution.—The NF compounds must be treated as very powerful explosives, which are extremely sensitive to impact and perhaps phase changes induced by changes in temperature! Thus explosions frequently occurred when the diaziridines were being condensed or volatilized. The use of certain cold baths, as discussed below, appeared to reduce the chance of explosion. The diaziridines appeared to be much more sensitive to detonation then the dangerous starting materials, pentafluoroguanidine and tetrafluoroformamidine. The NF compounds are also strong oxidizing agents.

The small scale of the experiments described below should be noted. Even at this scale, protective clothing, equipment for remote manipulation of apparatus, and suitable barricades were required.[18]

General.—The volatile reagents and products were manipulated in a vacuum line. Cesium fluoride and rubidium fluoride were used as obtained from the American Potash and Chemical Corp. Transfers of the metal fluorides were made in a drybox in order to avoid contact with atmospheric moisture. Samples of pentafluoroguanidine and tetrafluoroformamidine were kindly supplied by Drs. S. Frank and M. D. Meyers of these laboratories.[19] The reactions were carried out in Pyrex glass reactors. Joints and stopcocks were lubricated with Kel-F No. 90 grease.

3-Difluoramino-1,2,3-trifluorodiaziridine.—Pentafluoroguanidine (0.89 mmol) was vacuum transferred into a 27-ml reactor containing 5 g of rubidium fluoride at −132°. The bath was removed, and the reaction was allowed to proceed at room temperature for 3 hr. The product gas (1.0 mmol) was fractionated in a vacuum line using traps at −78, −132, and −196°. Some noncondensable gas was pumped through the trap at

---

[14] The observed pattern was temperature dependent. At ca. −60°, the peak at ϕ^* 92.9 was cleanly resolved into an AB pattern: ϕ_A^* 91.3, ϕ_B^* 93.9, J_{AB} = 150 cps. Also, additional weak spin–spin splitting was observed n the peaks at ϕ^* 91.3.

[15] W. T. Miller, Jr., J. H. Fried, and H. Goldwhite, *J. Amer. Chem. Soc.*, **82**, 3091 (1960), and references cited therein.

[16] W. T. Miller, Jr., W. Frass, and P. R. Resnick, *ibid.*, **83**, 1767 (1961).

[17] R. D. Dresdner, F. N. Tlumac, and J. A. Young, *J. Org. Chem.*, **30**, 3524 (1965).

[18] The various types of shielding to be used with such compounds have been described by C. L. Knapp [*Ind. Eng. Chem.*, **55**, No. 2, 25 (1963)] and D. R. Smith [*J. Chem. Educ.*, **41**, A520 (1964)].

[19] These materials were separated from the products obtained by fluorination, in a fluid bed, of biguanide.

−196°. Nothing condensed at −78°, 0.56 mmol condensed at −132°, and 0.30 mmol condensed at −196°. The noncondensable gas amounted to 0.14 mmol by difference.

Infrared and mass spectral analyses of the −196° condensate indicated that this fraction was a mixture of carbon tetrafluoride,[20] silicon tetrafluoride,[20] difluorodiazine (both isomers),[7] carbon dioxide, and impurities. The −132° condensate amounted to 0.22 mmol after purification by fractional codistillation. A −132° bath was used for condensing the diaziridine, because one sample exploded as it was being condensed at −196°. A number of runs under various conditions were made in order to accumulate enough material for characterization. The infrared spectrum at 12 torr in a 100-mm gas cell had bands at 7.26 (s), 7.91 (w), 9.75 (m), 10.10 (s), 10.9 (s, shoulder), 11.10 (s) 11.95 (w), and 13.6 μ (w, very broad).

Reaction of Tetrafluoroformamidine with Rubidium Fluoride.—Tetrafluoroformamidine (1.29 mmol) was condensed at −160° into a 50-ml reactor containing 5.0 g of rubidium fluoride. The bath was then removed and the reaction was allowed to proceed at room temperature for 3.0 hr. The product gas, largely a mixture of tetrafluorodiaziridine and the dimer, amounted to 0.89 mmol. Noncondensable gas (0.1 mmol) was pumped off at −196°. The remaining material was fractioned in the vacuum line using a −119° bath to condense the dimer (0.37 mmol), mol wt 214, 232 (calcd 232). The dimer amounted to 0.29 mmol after purification by fractional codistillation. The infrared spectrum of the dimer in the gas phase had bands at 7.1 (s), 7.7 (s), 8.0 (s), 8.2 (s), 8.6 (s), 9.7 (m), 10.2 (m), 10.6 (s), 11.0 (s), 12.3 (w), 12.8 (m), and 13.4 μ (m).

The 0.38 mmol of product which passed through the −119° trap was impure tetrafluorodiaziridine.

Several additional runs were made in which the amounts of tetrafluoroformamidine and the volume of the reactor were varied. The results seemed to indicate that both increasing the ratio of rubidium fluoride to tetrafluoroformamidine and decreasing the volume of the reactor favored formation of the dimer.

Dimerization of Tetrafluoroformamidine with Cesium Fluoride.—Tetrafluoroformamidine (0.94 mmol) was added by vacuum transfer to a 148-ml reactor containing 5.0 g of cesium fluoride at −160°. The reactor was allowed to warm spontaneously from −160° toward room temperature for 17 min. The product (0.48 mmol) condensed completely at −119° in a vacuum line. An infrared spectrum showed that the product was quite pure dimer, but a weak additional band at 6.2 μ was observed, as well as a weak absorption on the shoulder of the 7.1-μ band. These additional bands were not observed in the dimer obtained by using rubidium fluoride, as described above.

Tetrafluorodiaziridine.—Conditions necessary to prevent explosions of tetrafluorodiaziridine have not been fully defined. Several samples containing tetrafluorodiaziridine have exploded as they warmed from or were cooled to −160°. A higher condensation temperature or dilution with another compound, as described below, might be advantageous.

Bis(difluoramino)difluoromethane was used as a diluent in the following experiment. A mixture of bis(difluoramino)difluoromethane and tetrafluoroformamidine after fractional codistillation had a molecular weight (gas density) of 123. This mixture (1.65 mmol) was vacuum transferred into a 228-ml reactor containing 5.0 g of potassim fluoride. The product (1.56 mmol) after a reaction time of 17 hr at room temperature was largely tetrafluorodiaziridine and bis(difluoramino)difluoromethane according to an infrared spectrum and fractional codistillation analysis. The latter showed three peaks with relative areas: unidentified component, 1.4%; tetrafluorodiaziridine and bis(difluoramino)difluoromethane, 90.3%; dimer, 8.3%. The amount of dimer in the mixture was calculated as 11.5% from the decrease in mmoles of gas during the reaction. Correction of the observed molecular weight (135) for the amount of dimer present (average of 8.3 and 11.5 mol%) gave an approximate molecular weight of 124 for the mixture of tetrafluorodiaziridine and bis(difluoramino)difluoromethane. The close agreement between the molecular weights of the starting mixture and the product, after correction for dimer, strongly suggest that tetrafluoroformamidine and the product are isomers.

Tetrafluorodiaziridine was separated by fractional codistillation from this reaction product. Other samples of tetrafluorodiaziridine were obtained from reactions of tetrafluoroformamidine with potassium fluoride or rubidium fluoride in the absence of a diluent. Fractionation through a trap at −119° and condensation at −160° was used to isolate tetrafluorodiaziridine, which was then either combined with trichlorofluoromethane[21] or handled without diluent (caution). Tetrafluorodiaziridine was stored at the temperature of Dry Ice. Data was obtained on samples treated by these various methods. The infrared spectrum of a sample in the gas phase (8 torr in a 100-mm cell) had bands at 7.09 (s), 7.37 (s), 9.85 (m), 11.09 (s), 13.95 (w), and 14.20 μ (w).

Reaction of Tetrafluorodiaziridine (2) with Ferrocene.—Ferrocene (Aldrich Chemical Co., sublimed, 28.5 mg) was smeared around the walls of a 50-ml reactor with a few drops of Kel-F oil (tetramer), and *ca.* 0.09 mmol of tetrafluorodiaziridine was added by vacuum transfer. The reaction took place slowly at room temperature as shown by spectra taken after 1 and 4 days. After 2 weeks all of the diaziridine had reacted. Difluorodiazirine[13] and (probably) carbon tetrafluoride were observed in the infrared spectrum of the product gas.

Registry No.—Pentafluoroguanidine, 10051-06-6; tetrafluoroformamidine, 14362-70-0; **1**, 17224-08-7; **2**, 17224-09-8; **3b**, 17224-10-1.

Acknowledgment.—I should like to thank Mr. A. Struck for obtaining the mass spectral data and Dr. J. Lancaster and Mrs. M. Neglia for the nmr spectrra. I should also like to thank Dr. S. Frank and Dr. V. P. Wystrach for helpful suggestions and encouragement. Workers at Minnesota Mining and Manufacturing Co. provided some useful discussion concerning the structure of the dimer.

---

[20] D. G. Weiblen in "Fluorine Chemistry," Vol. II, J. H. Simons, Ed., Academic Press Inc., New York, N. Y., 1954, pp 469 and 498.

[21] Tetrafluorodiaziridine was volatilized at −119° and condensed into trichlorofluoromethane at −160°.