

The Polymerization of Difluorodiazirine

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Pyrolysis or ultraviolet photolysis of difluorodiazirine in the presence of boron trifluoride produced polydifluoromethylene. Like polymethylene derived from diazomethane, the polydifluoromethylene so produced possesses "living polymer" properties. The mechanism of polymerization is discussed and is thought to involve the formation of a linear intermediate.

Although the polymerization of diazo compounds, both fluorinated (1) and hydrocarbon (2), is well documented, there is no report of the formation of polymeric material from the isomeric diazirines (3). We now report the formation and physical properties of polydifluoromethylene derived from difluorodiazirine and discuss the possible mechanism of its formation.

Results and Discussion.

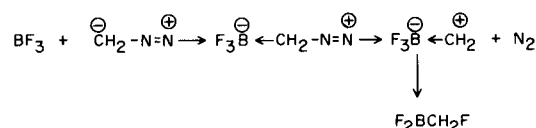
Unlike diazo compounds, difluorodiazirine does not polymerize in the presence of boron trifluoride under normal conditions. On the other hand, photolysis or pyrolysis of mixtures of boron trifluoride and difluorodiazirine, either in the gaseous state or in an inert solvent, produces a white solid, the infrared spectrum and X-ray powder photograph of which are identical with those of polytetrafluoroethylene.

The properties of the polymer obtained under various conditions are summarized in Table I. The yields and properties of the polymer produced are dependent upon the reaction conditions and also the amount of excess boron trifluoride employed.

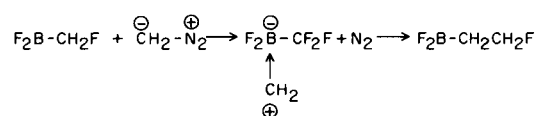
The most significant property of the polymer is that it is a "living polymer" (4) and retains the property of catalyzing further polymerization of difluorodiazirine, indicating the absence of any chain termination step in its formation.

Mechanism of Polymerization.

The mechanism of polymerization of diazomethane has been discussed at some length (2) and is thought to involve the coordination of ${}^{-}\text{CH}_2\text{-N=N}^+$ to boron trifluoride followed by nitrogen elimination and subsequent rearrangement. The isolation of $\text{BF}_2\text{CH}_2\text{F}$ from the reaction of diazomethane with an excess of boron trifluoride at low temperatures gives strong support for this mechanism (5).

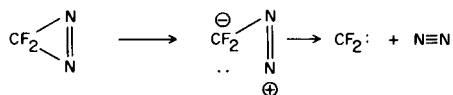


Further coordination at the boron atom followed by rearrangement produces polymer as shown below:



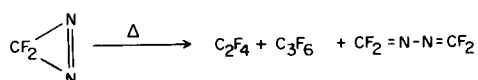
A characteristic of the above reaction is the "living polymer" property imparted by the ever present $\text{BF}_2\text{-CH}_2\text{-}$ end group, the catalytic properties of which remain unaffected by the length of the $\text{-CH}_2\text{-}$ chain. Since the polydifluoromethylene obtained from difluorodiazirine also possesses "living polymer" properties it seems likely that a similar mechanism involving the formation of a charged isomer of difluorodiazirine may be responsible for its formation. Hence, the focal point of any discussion of the mechanism of polymerization of difluorodiazirine is the mode of decomposition of the heterocycle under photolytic or pyrolytic conditions.

Although the products of pyrolysis or photolysis of difluorodiazirine have been characterized (6) the mechanism of its decomposition has not been discussed fully. It is apparent that difluorodiazirine can generate difluorocarbene when pyrolyzed or photolyzed either by the concerted elimination of nitrogen or by the cleavage of a C-N bond to form a linear intermediate which then decomposes by nitrogen elimination, *e.g.*

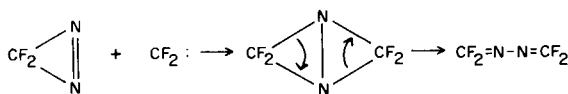


The nitrogen matrix photoisomerization of the hydrocarbon analog, diazirine, to diazomethane (7a) suggests the formation of a linear intermediate in this case, although the possibility of reaction of methylene with the nitrogen matrix can not be ignored (7b).

Some evidence for the formation of a linear intermediate during the decomposition of difluorodiazirine is indicated by the formation of tetrafluoro-2,3-diazabuta-1,3-diene, as well as tetrafluoroethylene and perfluorocyclopropane under certain conditions.



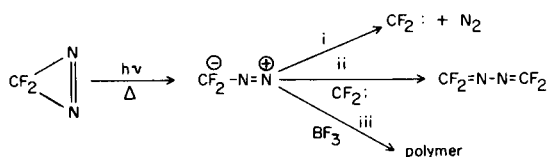
This compound could be derived either from reaction of difluorocarbene with the linear intermediate or by insertion of difluorocarbene into the difluorodiazirine double bond, followed by rearrangement as shown below:



We are unaware of any examples of insertion of difluorocarbene into an N=N bond, and hence favor the former reaction. Further support for the former reaction is the formation of formaldazine from the reaction of methylene with diazomethane (8).

That tetrafluoro-2,3-diazabuta-1,3-diene is not formed from the photolytic decomposition of difluorodiazirine at room temperature is due, presumably, to the excess energy imparted to the linear intermediate by the absorption of light causing it to decompose instantaneously. However, photolysis of difluorodiazirine in an argon matrix at 4.2°K produces the azine (9). In addition, photolysis of difluorodiazirine at -78° or -127° results in the formation of not only the azine but also diazadienes derived from it (10).

It is apparent that the photolysis or pyrolysis of difluorodiazirine in the presence of boron trifluoride involves three competitive reactions as shown below:

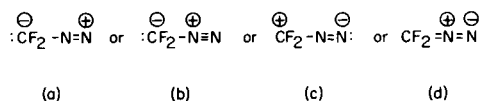


The yields of polymer obtained from the pyrolysis of mixtures of difluorodiazirine and boron trifluoride under various conditions are summarized in Figures 1 and 2. As would be predicted, increasing the temperature of pyrolysis decreases the stability of the linear intermediate favoring reaction (i) above, and causing a low yield of polymer. Increasing the concentration of boron trifluoride favors reaction (iii) and results in an increase in the yield of polymer.

Decreasing the temperature of pyrolysis also caused an increase in the ratio of $\text{CF}_2 = \text{N} - \text{N} = \text{CF}_2$ to C_2F_4 as would be expected.

Physical Properties of the Polymer.

Although the infrared spectrum and X-ray powder photograph of the polymer are identical with those of polytetrafluoroethylene the thermal stability is, in many cases, considerably lower and the elemental analysis shows the presence of varying amounts of both boron and nitrogen with concomitant lower carbon analysis (see Table I). The nitrogen content is considerably higher than that of polymethylene derived from diazomethane. This is possibly due to coordination occurring occasionally via nitrogen instead of carbon from the linear intermediate. Clearly, cleavage of the C-N bond in difluorodiazirine could produce various electronic distributions in the linear intermediate. The incorporation of nitrogen could



then be caused by coordination of tautomer (c) or (d) instead of (a) or (b). Certainly the possibility of such a reaction is more likely when the intermediate is being formed *in situ* than when it is in a stable equilibrated system as with diazomethane.

“Living Polymer” Properties.

The “living polymer” properties were demonstrated by the ability of the polymer to catalyze further polymerization of difluorodiazirine, or polymerization of an ethereal solution of diazomethane. The latter polymerization occurred rapidly even though the polymeric catalyst had previously been melted and resolidified under vacuum. If the mechanism described above is correct, the living polymer properties would be derived from a terminal $\text{BF}_2 - \text{CF}_2 -$ group. Although this system has previously been considered unstable [the “enduringly metastable” compound CF_3BF_2 has been reported (11)] we can offer no alternative suggestions.

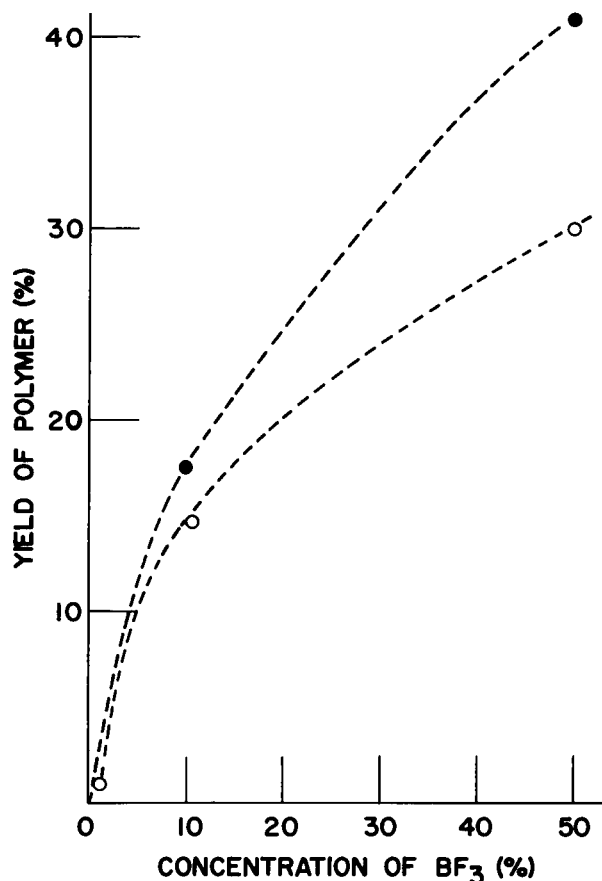


Figure 1

Pyrolysis of CF₂N₂ and BF₃

● at 140°

○ at 170°

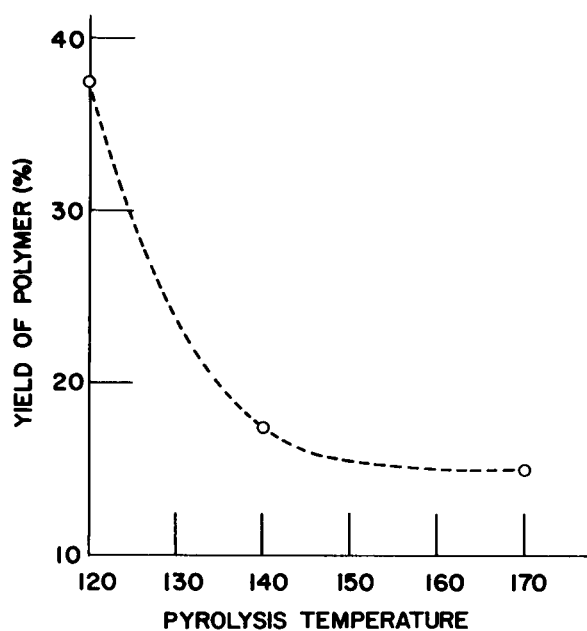


Figure 2

Pyrolysis of CF₂N₂ and BF₃

EXPERIMENTAL

Photolyses and pyrolyses were carried out in sealed Pyrex glass ampoules. Ultraviolet light was generated by a General Electric BH-6 lamp of 1,000 watts. Infrared spectra were measured on a Perkin-Elmer Model 21 double beam instrument using a 25 cm. gas cell fitted with sodium chloride windows for volatile samples, and either Nujol mulls or potassium chloride discs for solid samples. Vapor phase chromatographic separations were achieved using a 2-m. x 1/2-inch Kel-F8126 column and the products were isolated by condensing them from the effluent stream of gas at -196° in a trap filled with glass beads.

TABLE I

Ratio of BF ₃ : CF ₂ N ₂	Solvent	% Yield of Polymer	Melting Point	Elemental Analyses			
				C	F	B	N
1 : 10	CF ₂ ClCFCl ₂	60	230d	23.3	73.0	0.8	1.4
1 : 100	"		230				
Trace (a)	"	64	300	24.0	73.5		0.9
1 : 10	CH ₂ Cl ₂	26	170				
1 : 1	None (b)	30	212	22.9	74.2		
1 : 10	None (b)	15	230	23.4	74.4		
1 : 100	None (b)	1					
				Calcd. for (CF ₂) _n , C, 24.0; F, 76.0.			

(a) Obtained from "living polymer" (see text). (b) Indicates pyrolytic reaction, (at 170°), others are photolytic using a General Electric 1000-watt BH-6 lamp.

Photolysis of Difluorodiazirine with Boron Trifluoride.

(i) With Freon-113 as the Solvent.

Difluorodiazirine, CF_2N_2 , (0.35 g., 4.5 mmoles) and boron trifluoride, BF_3 , (0.03 g., 0.45 mmole) were condensed into a Pyrex tube containing Freon-113 (10 ml.) and photolyzed with ultraviolet light for 4 hours. After removal of the volatile material, a yellow solid remained (0.14 g., 60% theory yield of $(\text{CF}_2)_n$). The infrared spectrum and X-ray powder photograph of this material were identical with those of polytetrafluoroethylene, melting point, 250° dec.

Anal. Calcd. for CF_2 : C, 24.0; F, 76.0; N, 0.0; B, 0.0; Found: C, 23.3; F, 73.0; N, 1.4; B, 0.8.

(ii) With Methylene Chloride as the Solvent.

Difluorodiazirine, CF_2N_2 , (0.38 g., 4.9 mmoles) and boron trifluoride (0.033 g., 0.49 mmole) were condensed into a Pyrex tube together with methylene chloride (20 ml.) and irradiated with ultraviolet light for 8 hours. After removal of volatile material a mixture of yellow oil and white solid (0.0625 g., 26.0% theory $(\text{CF}_2)_n$) remained. The infrared spectrum of the white solid was identical with that of polytetrafluoroethylene.

(iii) Without Solvent.

Difluorodiazirine, CF_2N_2 , (0.382, 4.9 mmoles) and boron trifluoride (0.03 g., 0.45 mmole) were condensed into a 250 ml. gas bulb and irradiated with ultraviolet light for four hours. After removal of the volatile material which consisted of a mixture of tetrafluoroethylene, boron trifluoride, and nitrogen, a mixture of brown oil and white solid remained (0.05 g., 20% theory for $(\text{CF}_2)_n$) which were identified as $(\text{CF}_2)_n$ by their infrared spectra.

Photolysis of Difluorodiazirine in the Presence of Polydifluoromethylene.

Difluorodiazirine, (0.35 g., 4.5 mmoles) was condensed into a Pyrex tube containing Freon-113 (20 ml.) and a trace of the polymer described above and irradiated with ultraviolet light for four days. After removal of all volatile material a brown solid remained (0.143 g., 64% theory $(\text{CF}_2)_n$) the infrared spectrum and X-ray powder photograph of which were identical with those of polytetrafluoroethylene, melting point, 300° .

Anal. Calcd. for CF_2 : C, 24.0; F, 76.0; N, 0.0. Found: C, 24.9; F, 73.5; N, 0.9.

Catalysis of Polymerization of Diazomethane with "Living" Polydifluoromethylene.

Polymeric material from the above experiment was melted under vacuum and then resolidified. A small quantity (0.01 g.) was then added to a solution of diazomethane in ether. An immediate evolution of nitrogen occurred accompanied by the formation of a white precipitate which was identified subsequently as polymethylene by comparison of its infrared spectrum with that of an authentic sample.

Pyrolysis of Difluorodiazirine in the Presence of Boron Trifluoride.

Difluorodiazirine (0.382 g., 4.9 mmoles) and boron trifluoride (0.03 g., 0.49 mmole) were condensed into a Pyrex tube and

heated together at 140° for one hour. After removal of the volatile material which was found to consist of tetrafluoroethylene, perfluorocyclopropane, perfluoro-2,3-diazabuta-1,3-diene, boron trifluoride and nitrogen, a white solid remained (0.045 g. 18% theory $(\text{CF}_2)_n$) the infrared spectrum of which was identical with that of polytetrafluoroethylene, melting point, $200-210^\circ$.

Anal. Calcd. for CF_2 : C, 24.0; F, 76.0; Found: C, 23.4; F, 74.4.

Low Temperature Photolysis of Difluorodiazirine.

Difluorodiazirine (0.78 g., 10.0 mmoles) was condensed *in vacuo* into a Pyrex glass ampoule and photolyzed with ultraviolet light at -127° (*n*-propyl alcohol slush bath) for eight hours. The volatile products were then separated by fractional distillation-condensation and vapor phase chromatography, and identified as unreacted difluorodiazirine (9.5 mmoles) together with perfluoro-2,3-diazabuta-1,3-diene, (ca. 0.1 mmole), perfluoro-2,4-diazapenta-1,4-diene, (ca. 0.2 mmole), and perfluoro-2,5-diazahexa-1,5-diene (ca. 0.2 mmole), which were identified by comparison of their infrared spectra with those of authentic samples.

Acknowledgment.

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