

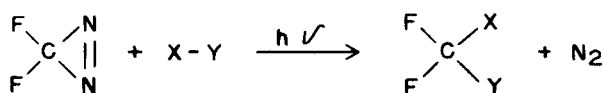
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Difluorodiazirine. II. Difluoromethane Derivatives (1)

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The photolysis of difluorodiazirine is a convenient technique for the formation of difluorocarbene. Difluorocarbene, generated in this manner, has been shown to react with chlorine, iodine, dinitrogen tetroxide and nitryl chloride to yield the corresponding difluoromethane derivatives.

The facile reaction of free radicals and carbenes with halogens has been recognized for some time. Recently, difluorocarbene was shown to react with chlorine (2a, b), bromine (2a), iodine (2b) and hydrogen chloride (2b) to form the corresponding difluoromethane derivatives. In the present investigation, difluorocarbene, generated by ultraviolet photolysis of difluorodiazirine (I) (3), was observed to react with chlorine, iodine, dinitrogen tetroxide and nitryl chloride.



I

II, X = Y = Cl

III, X = Y = I

IV, X = Y = NO₂

V, X = Cl, Y = NO₂

As can be seen from Table I, chlorine reacts very readily with difluorocarbene at room temperature to form dichlorodifluoromethane (II) when a gaseous mixture of chlorine and difluorodiazirine (2:1 molar ratio) is irradiated with ultraviolet light. The identity of II was established by a comparison of the infrared and F¹⁹ nuclear magnetic resonance spectra with those of an authentic sample.

In contrast to the reaction with chlorine, the reaction of difluorocarbene with iodine was carried out in solution in a sealed ampoule. Difluorodiiodomethane (III) was obtained in about a 21% yield when a solution of difluorodiazirine (I) and iodine in CF₂Cl₂ was exposed to wavelengths of ultraviolet light (4) of 3000-4000 Å. Minor quantities of 1,2-diiodotetrafluoroethane were also formed. Difluorodiiodomethane (2b) is a light yellow colored liquid exhibiting a vapor pressure of 13-14 mm. of Hg at 0°C., and showing a single peak at -19.4 φ* in the fluorine nuclear magnetic resonance spectrum. The infrared and ultraviolet spectra of CF₂I₂ are characterized by absorptions at 8.97 μ (s), 9.40 μ (s) and 13.49 μ (vs) and 298 mμ, respectively.

In a manner analogous to the reaction with chlorine, difluorodiazirine was allowed to react with dinitrogen tetroxide under photolytic conditions. The previously unreported difluoromethane derivative, difluorodi-

nitromethane (IV), was isolated in a 24% yield when ultraviolet wavelengths of 3000-4000 Å were employed. The decreased reactivity of dinitrogen tetroxide versus chlorine is shown by the formation of tetrafluoroethylene as the major product. Difluorodinitromethane (IV) exhibits a broad absorption with the maximum at 248 mμ in the ultraviolet spectrum.

The identity of difluorodinitromethane was established on the basis of its spectral characteristics and elemental analyses (*Anal.* Calcd. for CF₂N₂O₄: C, 8.5; F, 26.8; m.w., 142. Found: C, 9.0; F, 26.9; m.w., 141). In the fluorine nuclear magnetic resonance spectrum the CF₂ absorption is split into the expected five-fold peak (J = 11.4 c/s) centered at 84.1 φ* due to coupling with the nitrogen atoms of the two nitro groups. An absorption of strong intensity at 6.14 μ in the infrared spectrum is assigned to the asymmetric stretching vibration of the nitro group. Other absorptions are at 7.53 μ (s), 8.16 μ (s), 9.71 μ (m), 11.70 μ (w), 12.50 μ (s) and 14.34 μ (w).

The three possible products retaining a CF₂ moiety were all realized in the photolytic reaction of difluorocarbene with nitryl chloride; dichlorodifluoromethane (II, 70-80%), chlorodifluoronitromethane (V, 15%) and difluorodinitromethane (IV, 1-2%). Chlorodifluoronitromethane (V) has been described previously; however, spectral information was not published (5). The F¹⁹ nuclear magnetic resonance spectrum of V is characterized by a three-fold peak (J = 12.7 c/s) at 51.1 φ* and the nitro absorption is located at 6.20 μ (s) in the infrared spectrum. Other absorptions appear at 7.52 μ (m), 8.06 μ (s), 8.64 μ (s), 10.26 μ (s), 12.13 μ (s) and 14.03 μ (m).

It is interesting to note the correlation in vapor phase chromatography relative retention times and F¹⁹ nuclear magnetic resonance shielding values which can be utilized in the series, II, IV and V, to verify the structure assignments. Knowing the relative retention times and shielding values for the CF₂ group in dichlorodifluoromethane (II, Tr = 18.2, 6.9 φ*) and difluorodinitromethane (IV, Tr = 136.0, 84.1 φ*), one would predict the corresponding values for chlorodifluoronitromethane (V) to be about 77.1 and 45.5 φ*, respectively. The measured values are 75.5 and 51.1 φ*.

TABLE I

Difluoromethane Derivatives

Reactant	Molar Ratio (a)	Product	Yield, %	T _r (b)
Cl ₂	2	CF ₂ Cl ₂ (II)	90-95	18.2
I ₂	6	CF ₂ I ₂ (III)	21	149.0 (c)
N ₂ O ₄	5	CF ₂ (NO ₂) ₂ (IV)	24	136.0
ClNO ₂	10	CF ₂ Cl ₂ (II)	80	18.2
		CF ₂ ClNO ₂ (V)	15	75.5
		CF ₂ (NO ₂) ₂ (IV)	1-2	136.0

(a) Molar Ratio = moles reactant/moles CF₂N₂. (b) T_r = Relative retention time for vapor phase chromatography identification - $\frac{T_{\text{compound}} - T_{\text{air}}}{T_{\text{CFCl}_3} - T_{\text{air}}} \times 100$. (c) CCl₄ reference instead of CFCl₃.

EXPERIMENTAL

General.

The iodine (Merck and Co.), chlorine (Matheson Co.) and dinitrogen tetroxide (Matheson Co.) were used without further purification. The nitryl chloride was synthesized according to Freeman and Emmons (6).

Chromatographic analyses were performed with a Model 154-D Perkin-Elmer Vapor Fractometer. The analytical analyses and preparative scale separations were obtained using a 1/2" o.d. tube two meters long and packed with 33% KF-8126 (7) oil on celite.

Infrared spectra were obtained on a Perkin-Elmer Model 21 double beam instrument using a 2.5 cm. gas cell with NaCl windows. Fluorine nuclear magnetic resonance spectra were measured with a Varian V-4300-2 instrument operating at 40.0 mc. An internal standard of CFCl₃ was used for the determination of shielding values which are reported in phi (φ*) (8) units at dilutions of about 20-30%.

Synthesis of CF₂Cl₂, CF₂(NO₂)₂ and CF₂ClNO₂.

The same general procedure was common to the reactions of difluorodiazirine with chlorine, dinitrogen tetroxide and nitryl chloride. To a sample of difluorodiazirine (I, 0.078 g., 1.0 x 10⁻³ moles), contained in a 580 cc. gas bulb at liquid nitrogen temperature was added the appropriate molar ratio (See Table I) of coreactant by vacuum transfer techniques. After degassing and warming to ambient room temperature, the mixture was irradiated for 16-20 hours with a General Electric BH-6 ultraviolet light source fitted with a Corning No. 5840 filter (4). Preliminary separation of the difluoromethane derivative from the excess reactant could sometimes be accomplished by simple fractional distillation-condensation techniques. Preparative vapor phase chromatography (Table I) was employed for the final purification. The reported yields represent the quantity of pure difluoromethane which was separated from the reaction mixture by vapor phase chromatographic trapping techniques.

Difluorodiiodomethane.

Into a 10 cc. glass ampoule which contained 0.762 g. (6 x 10⁻³ moles) of iodine was condensed 7 cc. of CF₂Cl₂ (solvent) and 0.078 g. (1 x 10⁻³ moles) of difluorodiazirine. The ampoule was sealed and warmed to 25° and the liquid phase was irradiated for 16 hours with a General Electric BH-6 ultraviolet lamp fitted with a Corning No. 5840 filter. The entire mixture was fractionated through -78° and -196°C. receivers after the irradiation period. The -78°C. trap contained about 3 x 10⁻⁴ moles of III contaminated with a small amount of 1,2-diiodotetrafluoroethane. Final purification by preparative vapor phase chromatography afforded a 20.7% yield of pure difluorodiiodomethane (III).

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