

Contribution No. 305 from the Central Research Laboratories
Minnesota Mining and Manufacturing Company

Difluorodiazirine. IV. Synthesis of Substituted Perfluorocyclopropanes (I)

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The preparation of eight previously undisclosed substituted perfluorocyclopropanes by the addition of difluorocarbene to the respective fluorocarbon olefins is described. The yields, generally 30-85%, are dependent upon the reaction temperature, the amount of excess olefin and the nature of the groups present in the fluoroolefin.

INTRODUCTION

The addition of difluorocarbene, generated by photolysis or pyrolysis of difluorodiazirine (2), to olefins to form difluorocyclopropanes has been reported (3). In some further studies which are the subject of this paper, this technique has been extended to the preparation of a family of substituted fluorocyclopropanes. The synthesis of hexafluorocyclopropane has been reported by several workers (4), and after completion of the present work Mahler described the preparation of a second member of this family, a novel perfluorobicyclobutane, by the double addition of difluorocarbene to hexafluoro-2-butyne (5).

RESULTS AND DISCUSSION

The ultra-violet photolysis of difluorodiazirine (I) at room temperature results in high yields of tetrafluoroethylene (2) according to equation (1). The further addition of the electrophilic difluorocarbene to this olefin to form hexafluorocyclopropane apparently does not occur because of the decrease in electron density at the double bond resulting from fluorine substitution. However, at higher temperatures (6) hexafluorocyclopropane is the major product (2).

Thus, it was not surprising to find that under photolytic conditions at room temperature, difluorocarbene adds to hexafluoropropene to form perfluoromethylcyclopropane (II) in only 4% yield.

As is to be expected, tetrafluoroethylene is the only by-product at this temperature. On the other hand, hexafluoropropene and difluorodiazirine when heated in the same molar ratio (10:1) at 150°C. for 4.5 hours afforded a 30% yield of II. In this case the by-products were identified as tetrafluoroethylene and hexafluorocyclopropane. Perfluoromethylcyclopropane (II) has not been described previously; its identity was established on the basis of spectral considerations and its elemental analyses. In the fluorine nuclear magnetic resonance spectrum of II (Table II), the CF_3 group appears as a doublet of five-fold peaks ($J = 9.5$ and 6.7 c/s, respectively) at $70.5 \phi^*$ (7) due to spin-spin coupling with the fluorines of the CF and two CF_2 groups, respectively. As a result of similar couplings, the fine structure of the CF_2 absorption is a doublet of four-fold peaks ($J = 2.8$ and 6.8 c/s) and the CF is a quadruplet of

five-fold peaks ($J = 9.4$ and 2.8 c/s) at the positions listed in Table II. In this case, the expected AB pattern of the CF_2 groups is not observed.

In the reaction of 1,2-dichloro-1,2-difluoroethylene (a 1:1 cis-trans mixture) with difluorodiazirine (I) at 150-160°C., stereospecific (3) addition of difluorocarbene gives 1,2-dichlorotetrafluorocyclopropane (47% yield). Although the two isomers, III and IV, were not separable by vapor phase chromatography, the fluorine nuclear magnetic resonance spectrum (Table II) of the mixture clearly differentiates between the two and attests to the fact that the original isomeric distribution (1:1) was retained.

The spectrum of the cis-isomer (III) is characterized by an AB type pattern for the CF_2 group due to the non-equivalence of the two fluorine atoms. Further splitting into triplets ($J = 5.3$ and 5.0 c/s) is observed for the peaks of the AB pattern. The CF absorption in III is also split into a triplet ($J = 5.2$ c/s) by the CF_2 moiety. The equivalent nature of the fluorine atoms in the CF_2 group of the trans-isomer (IV) results in single absorptions for both the *gem* fluorines and the CF moiety. In detail, each peak is a triplet ($J = 3.0$ and 2.8 c/s, respectively).

In a manner analogous to the reaction with 1,2-dichloro-1,2-difluoroethylene, difluorodiazirine (I) was allowed to react with trifluoroethylene, chlorotrifluoroethylene, trifluoroacrylonitrile and methoxytrifluoroethylene (8) at 150-160°C. The corresponding cyclopropanes, pentafluorocyclopropane (V, 65%), chloropentafluorocyclopropane (VI, 85%), cyanopentafluorocyclopropane (VII, 66%), and methoxypentafluorocyclopropane (VIII, 72%) were all identified by infrared and nuclear magnetic resonance spectroscopy and elemental analyses. The F^{19} nuclear magnetic resonance spectra of the CF_2 groups in the above cyclopropanes were interpreted on the basis of AB type patterns. No detailed analyses of the CF_2 absorptions were attempted because of their complex nature. The single CF absorption in chloropentafluorocyclopropane (VI), cyanopentafluorocyclopropane (VII) and methoxypentafluorocyclopropane (VIII) is characterized by further splitting into a triplet of triplets by coupling to the two pairs of fluorine in the CF_2 groups. The fluorine nuclear magnetic resonance absorption of the CFH moiety in pentafluorocyclopropane (V) appears at $238.5 \phi^*$.

The structure of this peak is a double triplet of triplets with J values of 55.0 c/s, 8.4 c/s and 4.5 c/s, respectively. The large coupling value is associated with the hydrogen and the triplets with the two pairs of identical fluorine atoms in the CF_2 structures.

1,1-Dichlorotetrafluorocyclopropane (IX) was synthesized in a 38% yield by the photolysis of a mixture of 1,1-dichloro-2,2-difluoroethylene and difluorodiazirine (15:1 molar ratio) at room temperature. A single CF_2 absorption at 144.3 cm^{-1} in the F^{19} nuclear magnetic resonance spectrum, satisfactory elemental analyses and a band at 6.68μ in the infrared spectrum support the assigned structure.

In regard to the infrared spectra of the various fluorocyclopropanes synthesized in this work, the most characteristic feature was an absorption of medium to medium-strong intensity in the $6.54 - 6.86 \mu$ region (9). The following band positions were measured; II (6.55μ), V (6.54μ), VI (6.62μ), VII (6.61μ), VIII (6.86μ), and IX (6.68μ).

In the case of VIII, the exact position of the absorption is more uncertain because of the absorption due to the methyl group.

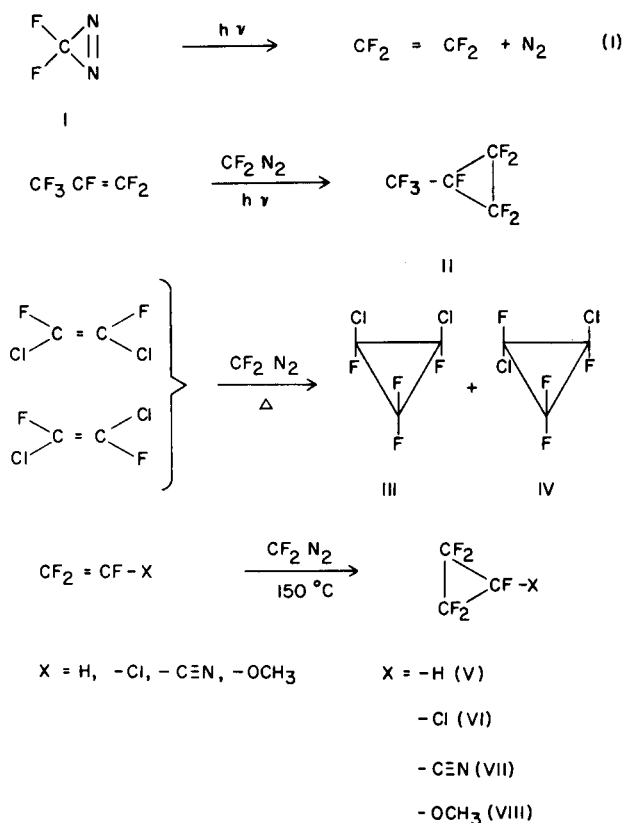


TABLE I
Substituted Perfluorocyclopropanes

Olefin	Cyclopropane	Molar Ratio (a)	Yield, %	Analyses	
				Calcd.	Found
$\text{CF}_2=\text{CFCF}_3$	CFCF_3 (II)	10	30 (4 b)	C, 24.0 F, 76.0	24.1 75.8
$\text{CFCl}=\text{CFCl}$	CF_2 (III) (IV)	10	47	C, 19.7 F, 41.5	20.0 41.5
$\text{CF}_2=\text{CFH}$	CFH (V)	4	65	C, 27.3 F, 72.0	27.2 72.9
$\text{CF}_2=\text{CFCl}$	CFCl (VI)	5	85	C, 21.7 F, 57.2	21.5 57.5
$\text{CF}_2=\text{CF}-\text{C}\equiv\text{N}$	$\text{CF}-\text{C}\equiv\text{N}$ (VII)	5	66 (15 b)	C, 30.6 F, 60.5	30.4 59.5
$\text{CF}_2=\text{CF}-\text{OCH}_3$	$\text{CF}-\text{OCH}_3$ (VIII)	5	72	C, 29.6 F, 58.6	29.5 58.0
$\text{CF}_2=\text{CCl}_2$	CCl_2 (IX)	15	38 (b)	C, 19.7 F, 41.5	19.5 41.2

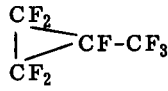


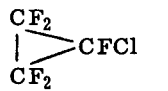
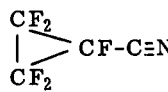
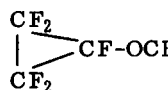
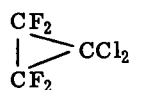
(a) Molar ratio = moles of olefin/moles of CF_2N_2 . (b) Reaction run at 25°C . using ultraviolet irradiation.

TABLE II
Nuclear Magnetic Resonance Spectra

Formula	Group	ϕ^*	
$\begin{array}{c} \text{CF}_2 \\ \\ \text{CF}_2 \end{array} \text{CFCF}_3 \text{ (II)}$	CF ₃	70.5	- no AB pattern
	CF ₂	154.1	
	CF	218.2	
$\begin{array}{c} \text{Cl-CF} \\ \\ \text{Cl-CF} \end{array} \text{CF}_2 \text{ (cis) (III)}$	CF ₂	{ 139.4 152.8 }	$J_{AB} = 172.5 \text{ c/s}$
	CF	165.3	
$\begin{array}{c} \text{Cl-CF} \\ \\ \text{Cl-CF} \end{array} \text{CF}_2 \text{ (trans) (IV)}$	CF ₂	145.4	
	CF	156.8	
$\begin{array}{c} \text{CF}_2 \\ \\ \text{CF}_2 \end{array} \text{CFH (a) (V)}$	CF ₂	{ 148.6 158.5 }	$J_{AB} = 207.4 \text{ c/s}$
	CF	238.5	
$\begin{array}{c} \text{CF}_2 \\ \\ \text{CF}_2 \end{array} \text{CFCl (VI)}$	CF ₂	{ 148.3 154.8 }	$J_{AB} = 187.8 \text{ c/s}$
	CF (b)	171.2	
$\begin{array}{c} \text{CF}_2 \\ \\ \text{CF}_2 \end{array} \text{CF-C}\equiv\text{N (VII)}$	CF ₂	{ 147.3 153.6 }	$J_{AB} = 189.2 \text{ c/s}$
	CF (c)	212.8	
$\begin{array}{c} \text{CF}_2 \\ \\ \text{CF}_2 \end{array} \text{CFOCH}_3 \text{ (d) (VIII)}$	CF ₂	{ 155.9 158.6 }	$J_{AB} = 196 \text{ c/s}$
	CF	165.7	
$\begin{array}{c} \text{CF}_2 \\ \\ \text{CF}_2 \end{array} \text{CCl}_2 \text{ (IX)}$	CF ₂	144.3	

(a) Proton absorption is at 5.14 τ and shows a double triplet with J values of 55.0 c/s and 12.7 c/s. The large coupling value is associated with the fluorine of the single CF and the triplet with one pair of identical fluorine in the CF₂ structure. The other pair does not show any measurable coupling. (b) The single CF shows a rough five-fold peak which is more exactly a triplet of triplets with approximately the same J value of 5.5 c/s. (c) The fine structure of the single CF is a triplet of triplets (J = 7.0 and 4.2 c/s) as caused by coupling to the two pairs of fluorine of the CF₂ groups. (d) The CF₂ absorption was analyzed as an AB type pattern using the center of the peaks. All absorptions show further fine structure. The CF absorption is recorded as the center of the observed multiplet.

TABLE III
Vapor Phase Chromatography Data

Olefin	T _r (a)	Cyclopropane	T _r
CF ₂ =CFCF ₃	8.8		14.8
CFCl=CFC1	106.0		187.0
CF ₂ =CFH	4.2		15.4
CF ₂ =CFC1	18.4		39.6
CF ₂ =CF-C≡N	42.2		54.4
CF ₂ =CF-OCH ₃	49.0		104.0
CF ₂ =CCl ₂	96.8		181.6

$$(a) \quad T_r = \text{Relative Retention Time} = \frac{T_{\text{compound}} - T_{\text{air}}}{T_{\text{CFCl}_3} - T_{\text{air}}} \times 100.$$

EXPERIMENTAL

General.

Chromatographic analyses were performed with a Model 154-D Perkin-Elmer Vapor Fractometer, utilizing a fluorocarbon type stationary phase. 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 (10) 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 and proton nuclear magnetic resonance spectra were measured with a Varian V-4300-2 instrument operating at 40.0 mc.; internal standards of CFC1₃ and (CH₃)₄Si were used for the determination of shielding values. The shielding values are reported in phi (φ*) (7) and tau (τ) (11) units for fluorine and proton, respectively, at dilutions of 20-30% by volume.

Synthesis of Cyclopropanes.

The mixture of difluorodiazirine (I) and excess fluoroolefin, contained in a 500 cc. glass storage bulb or a 20 cc. heavy wall glass ampoule, was either irradiated with a Hanovia 125-watt ultraviolet lamp at room temperature for approximately 20 hours or heated at 150-160°C. for 3-5 hours. Preparative vapor phase chromatography (Table III) was employed to separate the reaction mixture into its pure components. The yields and analyses for the fluorocyclopropanes are listed in Table I. The yields represent the quantity of pure product which was obtained by chromatographic trapping techniques.

Acknowledgments.

The author wishes to express his appreciation to Mr. D. P. Babb for his excellent technical assistance, Dr. J. J. McBrady for infrared and nuclear magnetic resonance measurements and interpretation, Mr. P. B. Olson for analytical determinations and Dr. J. G. Erickson for reviewing and editing the manuscript.

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Received December 7, 1964

St. Paul, Minnesota