## BRIEF COMMUNICATIONS

# REACTIONS OF DIFLUOROCARBENE WITH CONJUGATED POLYFLUORODIENES

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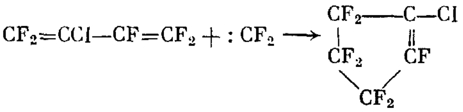
*Heating 2-chloroperfluoro-1,3-butadiene or perfluoro-1,3-pentadiene with excess hexafluoropropylene oxide leads to the formation of the corresponding cyclopentenes.*

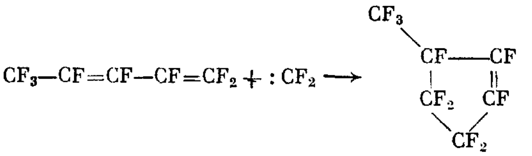
Mitch and Neuwar [1] have shown that difluorocarbene (DFC) generated upon the decomposition of difluoroaziridine at 130-140°C over 3-4 h reacts with perfluoro-1,3-butadiene to give a mixture of perfluorovinylcyclopropane (I) and perfluorocyclopentene (II).

We have found that DFC formed upon the thermolysis of readily available hexafluoropropylene oxide (HFPO) [2] adds to conjugated fluorodienes to give exclusively cyclopentenes. Thus, heating 2-chloroperfluoro-1,3-butadiene (III) with excess HFPO at 180-200°C over 5 h gave 1-chloroperfluoro-1-cyclopentene (IV) in 70-80% yield.



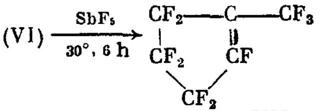
(III) (IV) (70—80%)

The addition of DFC to perfluoro-1,3-pentadiene (V) leads to the formation of perfluoro-2-methyl-1-cyclopentene (VI).



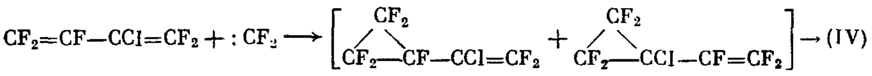
(V) (VI) (70%)

Cyclopentene (VI) isomerizes upon the action of $SbF_5$ to give perfluoro-1-methyl-1-cyclopentene (VII).



(VII)

Mitch and Neuwar [1] showed that heating (I) at 190°C leads to its isomerization to (II). In light of this result, we may propose that the reaction of DFC with conjugated dienes (IV) and (VI) occurs by the following scheme in the case of (IV)



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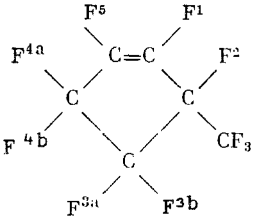
## EXPERIMENTAL

The $^{19}F$ NMR spectra were taken in $CDCl_3$ on a Bruker WP-200 SV spectrometer with $CF_3CO_2H$ as the external standard. The chemical shifts are given in ppm and the coupling constants are given in Hz. The Raman spectra were taken on a Ramanor spectrometer with excitation by an argon laser at 5145 Å. The mass spectra were taken on a V6-7070E mass spectrometer at 70 eV. The ion source temperature was 150°C.

**1-Chloroperfluoro-1-cyclopentene (IV).** A mixture of 10.0 g (60 mmoles) diene (III) and 40.0 g (240 mmoles) HFPO was heated in an autoclave at 190°C for 5 h. The autoclave was then opened. The gaseous products were distilled off. The residual liquid was distilled to give 9.3 g (73%) (IV). The $^{19}F$ NMR spectral data correspond to the data given by Feeney et al. [3].

**Perfluoro-2-methyl-1-cyclopentene (VI).** By analogy to the previous procedure, heating a mixture of 10.6 g (50 mmoles) diene (V) and 30.0 g (180 mmoles) HFPO at 190°C for 5h gave 9.0 g (69%) (VI), bp 48-49°C. $^{19}F$ NMR spectrum:



$64{,}5\,(F^1)$, $99{,}5\,(F^2)$, $-2{,}4\,(CF_3)$, $46{,}2\,(F_a^{3})$, $49{,}3\,(F_b^{3})$, $37{,}0\,(F_a^{4})$, $41{,}6\,(F_b^{4})$, $67{,}8\,(F_5)$; $J_{F^1-F^2} = 24$, $J_{F^1-CF_3} = 12$, $J_{CF_3-F^3_{a(b)}} = 15$, $J_{F^5-F^4_{a(b)}} = 12$, $J_{F_a^3-F_b^3} = J_{F_a^4-F_b^4} = 249$ Hz.

Raman spectrum: $\nu_{C=C}$ 1765 $cm^{-1}$. Mass spectrum (relative intensity, %) $[M^+]$ 262 (17.3), $[C_6F_9]^+$ 243 (62), $[C_5F_7]^+$ 193 (100), $[C_4F_6]^+$ 162 (15), $[C_4F_5]^+$ 143 (47), $[C_3F_5]^+$ 131 (28), $[CF_3]^+$ 69 (64). Found: C, 23.98; F, 72.94%. Calculated for $C_6F_{10}$: C, 26.92; F, 73.08%.

**Isomerization of (VI) by the Action of $SbF_5$.** A mixture of 0.1 g $SbF_5$ and 0.5 g (IV) was placed into an NMR tube and maintained at 30°C. After 6 h, the reaction mixture contained only $SbF_5$ and (VII) identified with an authentic sample by gas-liquid chromatography and $^{19}F$ NMR spectroscopy.

## LITERATURE CITED

1. R. A. Mitch and E. W. Neuwar, J. Phys. Chem., 70, No. 2, 546 (1966).
2. P. B. Sargent and C. G. Krespan, J. Am. Chem. Soc., 91, 415 (1969).
3. J. Feeney, Z. H. Sutcliffe, and S. H. Walker, Mol. Phys., 11, No. 2, 129 (1966).