structure IIa, was utilized for further synthesis (*Anal.* Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.95; H, 8.31). Bis-2,4-dinitrophenylhydrazide, m.p. 238–239° (*Anal.* Calcd for $C_{24}H_{28}N_4O_4$: C, 52.17; H, 4.35; N, 20.29. Found: C, 51.85; H, 4.38; N, 20.46). Dioxime (IIb), m.p. 228–229°. (*Anal.* Calcd for $C_{12}H_{18}N_2O_2$: C, 64.91; H, 8.10; N, 12.61. Found: C, 64.51; H, 8.29; N, 12.51). The dioxime (IIb) was converted to the di-*p*-toluenesulfonate (IIc), m.p. 141–142° (*Anal.* Calcd for $C_{26}H_{30}N_2O_6S_2$: C, 58.95; H, 5.64; N, 5.26. Found: C, 58.14; H, 5.62; N, 5.28). Solvolytic Beckmann rearrangement of IIc under alkaline conditions afforded 5,7-diacetamidobicyclo[2,2,2]-2-octene (IId), m.p. 260–261° (*Anal.* Calcd for $C_{12}H_{18}N_2O_2$: C, 64.91; H, 8.10; N, 12.61. Found: C, 64.20; H, 8.11; N, 12.62). Alkaline hydrolysis to the diamine (IIe) and quaternization with methyl iodide and sodium hydroxide afforded the dimethiodide (IIf) (*Anal.* Calcd. for $C_{14}H_{28}N_2I_2$: C, 35.18; H, 5.85; N, 5.85. Found: C, 34.53; H, 6.07; N, 5.26). Pyrolysis of the derived dimethohydroxide at 90–110° yielded an oil. Macro vapor phase chromatography of this (TCP, 1 inch × 6 ft., 300 cc. N_2/min., 15 mm. outlet press., 75° column) afforded as a minor product benzene (time 3.5 min.), identified by its infrared spectrum and as the major product barrelene (I) (37% based on dimethiodide; time 14 min.). Barrelene thus obtained melted at 15.0–16.0° (*Anal.* Calcd for C_8H_8: C, 92.30; H, 7.70. Found: C, 92.60; H, 7.73).

Infrared: ($CHCl_3$) strong peaks only at 3.29, 3.39, 6.34, 7.50, 9.80, 11.11, 12.35, 14.30 (broad and intense) microns; also 6.20 wk; in CS_2 also 8.20 microns. Ultraviolet: $\lambda_{\max} = 208.0$ mmu ($\log \epsilon$ 3.05), 239 mmu (2.48) in ethanol at 4.99×10^{-4} m./lit.

N.m.r.[5]: (*cf.* Table I) the vinyl hydrogen (at C-2) absorption was split (J_{12}) by spin coupling with the C-1 bridgehead hydrogen and split again (J_{13}) by weaker coupling with the C-4 hydrogen, thus giving the observed quartet. The bridgehead hydrogen absorption was split into a quartet by three adjacent (C-2, C-6, C-7) hydrogens and each component was split again into a quartet by coupling with the three equivalent hydrogens one carbon more removed. This sixteen component pattern is predicted nicely (Table I; values in parentheses) by use of the equation $\bar{\nu} = 91.1 \pm nJ_{12} \pm mJ_{13}$ cps., where 91.1 cps. is the center of the sixteen component pattern, $J_{12} = 2.10$ cps. and $J_{23} = 1.50$ cps. are taken from the vinyl quartet, and where n and m are independently = $^1/_2$ or $^3/_2$. The area under the peaks was in the ratio of 2.95:1 as expected.

TABLE I[a]

NUCLEAR MAGNETIC RESONANCE DATA

Vinyl H Peaks: 134.0, 132.7, 132.1, 130.4 (all very strong). Bridgehead Peaks: 96.7, (96.5), 95.0 (95.0), 94.4 (94.4), 93.3 (93.5), 92.9 str. (92.9 str.), 92.4 (92.3), 92.0 (92.0), 91.3 str. (91.3 str.), 90.5 str. (90.9 str.) 90.2 (90.2), 89.8 (89.9), 89.2 str. (89.3 str.), 88.6 (88.7), 87.7 (87.8), 87.1 (87.2), 85.7 (85.7).

[a] C.p.s. downfield from tetramethylsilane; predicted values in parenthesis; run at 40 mc.

Hydrogenation in ethanol with PtO_2 proceeded with constant uptake to 92% of the theoretical, giving bicyclo[2,2,2]octane, m.p. 171–172° after vapor phase chromatography (only one peak), identified also by infrared.

In contrast to bicyclo[2,2,2]-2,5-octadiene, reported by Grob[6] largely to decompose to benzene and ethylene, barrelene was recoverable (isolative vapor chromatography) to the extent of at least 71% after heating to 200° for 24 hr. At 250° it decomposed to benzene and acetylene.

Simple LCAO MO calculations show that were 2,6-overlap as effective as 2,3-overlap, barrelene would have the same delocalization energy (2β) as benzene. However, calculation suggests only 22.5% as much overlap, leading to the prediction that barrelene should have no delocalization energy, although the six pi electrons appear in three delocalized orbitals (deg. pair at 1.225β and one at 0.55β; note β is neg.) Thus barrelene is subject to electron delocalization without the usually attendant delocalization energy. The ultraviolet bands probably arise from electron excitation from the 0.55β orbital to two orbitals centering about a -0.775β degenerate pair predicted by the simple Hückel calculations.

This research together with the results of further investigations will be reported in more detail later.

The authors acknowledge some exploratory research on the problem by Dr. B. S. Thyagarajan. Also, acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research.

NOTE ADDED IN PROOF.—We have learned by private communication that C. G. Krespan, B. C. McKusick and T. L. Cairns have prepared a tetramethylbis-(trifluoromethyl)-barrelene. Also Professor S. Winstein has communicated the results of calculations due to appear shortly in THIS JOURNAL, in which absorption bands at 241 and 214 mμ are predicted for barrelene.

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[5] We thank Mr. C. Creswell for running the n.m.r. spectra.

[6] C. A. Grob, H. Kny and A. Gagneux, *Helv. Chim. Acta*, **40**, 130 (1957).

CHEMISTRY DEPARTMENT HOWARD E. ZIMMERMAN
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS ROBERT M. PAUFLER

RECEIVED DECEMBER 28, 1959

DITHIETENE AND BICYCLOÖCTATRIENE RING SYSTEMS FROM BIS-(FLUOROALKYL)-ACETYLENES

Sir:

Bis-(fluoroalkyl)-acetylenes have been found to undergo addition reactions with sulfur and phosphorus to form new types of cyclic compounds and with aromatic compounds to form bicycloöctatriene derivatives.

Thus, when hexafluoro-2-butyne[1] was passed through vapors of boiling sulfur under atmospheric pressure, bis-(trifluoromethyl)-1,2-dithietene (I) was obtained in 80% yield. The dithietene is a yellow liquid; b.p. 95–96°; $\lambda_{\max}^{\text{isooctane}}$ 238 mμ (ε 7440), 340 mμ (ε 80). Strong infrared absorp-

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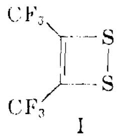
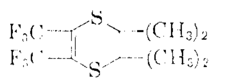
[1] A. L. Henne and W. G. Finnegan, THIS JOURNAL, **71**, 298 (1949).



I

tion at 6.14 μ indicates C=C. Other spectral data, including nuclear magnetic resonance, are also consistent with the dithietene structure (I). The thermal stability of the dithietene indicates that it has the aromatic character implied by its structure, which satisfies Hückel's rule. *Anal.* Calcd. for $C_4F_6S_2$: C, 21.2; F, 50.4, S, 28.4; mol. wt., 226. Found: C, 21.4; F, 51.0; S, 28.1; mol. wt. (mass spec.), 226.

The diethietene adds to tetramethylethylene at 100° during 20 hours to give a 47% yield of a dihydrodithiin (II), b.p. 84° (4 mm.), m.p. 21–22°, and it adds similarly to ethyl vinyl ether, diethylacetylene, and other unsaturates. A trace of triethylamine dimerizes the dithietene to III, m.p. 111–112°. Although the dithietene is unstable with respect to this dimer at room temperature, the dithietene is the more stable species at temperatures near 200°.



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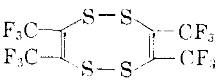
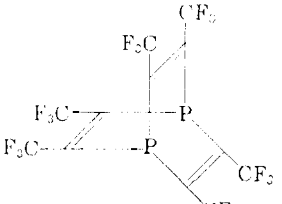
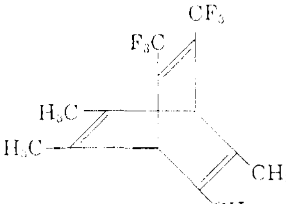


III

A different type of reaction occurs when red phosphorus is heated with hexafluoro-2-butyne (2:1 mole ratio) at 200° for 5 hours in the presence of a small amount of iodine. Hexakis-(trifluoromethyl) - 1,4 - diphosphabicyclo[2.2.2]octa - 2,5,7-triene (IV) is obtained in 45% yield as a colorless solid, m.p. 119–120° (recrystallized from acetic acid, then sublimed at 100° (1 mm.)); λ_{max}^{MeCN} 262 mμ (ε 450), 316 mμ (ε 640); infrared absorption at 6.22 μ (C=C). *Anal.* Calcd. for $C_{12}F_{18}P_2$: C, 26.3; F, 62.4; P, 11.3; mol. wt., 548. Found: C, 27.0; F, 62.4; P, 11.5; mol. wt. (mass spec.), 548.



IV

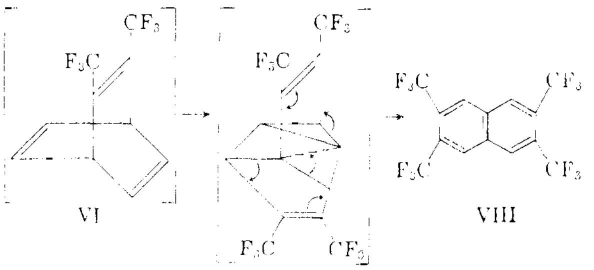


V

Hexafluoro-2-butyne also reacted with durene (1.3:1 mole ratio) at 200° for 10 hours to form 2,3,5,6 - tetramethyl - 7,8 - bis - (trifluoromethyl) - bicyclo[2.2.2]octa-2,5,7-triene (V) in 41% yield. We believe that this is the first time the ring of a simple benzene derivative has served as the diene in a normal Diels–Alder reaction. The bicyclooctatriene[2] thus formed is a colorless solid, m.p. 56–57° (from aqueous methanol). *Anal.* Calcd. for $C_{14}H_{14}F_6$: C, 56.8; H, 4.8; F, 38.5; mol. wt., 296. Found: C, 56.8; H, 5.1; F, 38.6; mol. wt. (mass spec.), 296. The ultraviolet spectrum showed $\lambda_{max}^{isooctane}$ 223 mμ (shoulder; ε 440), 287 mμ (ε 70). Comparison of the ultraviolet spectrum of V with spectra of molecules containing isolated double bonds that bear CF_3 groups leads us to believe that the absorption at 287 mμ is due to the $F_3C\overset{|}{C}{=}\overset{|}{C}CF_3$ group. The shoulder at 223 mμ can be explained as the lower-energy component of the split absorption arising from dipolar resonance interaction between the other two double bonds. Infrared and n.m.r. spectra are consistent with the assigned structure, as is the formation of 1,2-dimethyl-4,5-bis-(trifluoromethyl)-benzene and durene when the compound is heated at 250°.

Molecular orbital calculations in which the effect of fluoroalkyl groups is assumed negligible have been made by R. E. Merrifield of this laboratory; they indicate that V has vanishing delocalization energy independent of whether or not there is any overlap interaction between the double bonds.

An even more surprising reaction occurred when hexafluoro-2-butyne and an excess of benzene were heated at 250° for 12 hours. The principal products were 1,2-bis-(trifluoromethyl)-benzene (8%) and 2,3,6,7-tetrakis-(trifluoromethyl)-naphthalene (VIII) (30%), m.p. 173–174°. The formation of these products can be rationalized by assuming the intermediate formation of the bicyclooctatriene, VI. Thus, pyrolysis of VI should yield 1,2-bis-(trifluoromethyl)-benzene, while addition of hexafluoro-2-butyne to VI in the manner that tetracyanoethylene adds to bicycloheptadiene[3] should give VII; a shifting of electrons would convert VII to the 9,10-dihydronaphthalene, which would give the tetrakis-(trifluoromethyl)-naphthalene, VIII, on loss of hydrogen.



VI VII VIII

Extensions of these reactions to selenium and arsenic, to other aromatic compounds, and to other bis-(fluoroalkyl)-acetylenes will be described in more detailed papers on this research.

CONTRIBUTION NO. 599 FROM C. G. KRESPAN
THE CENTRAL RESEARCH DEPARTMENT
EXPERIMENTAL STATION B. C. MCKUSICK
E. I. DU PONT DE NEMOURS AND COMPANY
WILMINGTON, DELAWARE T. L. CAIRNS

RECEIVED JANUARY 25, 1960

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(2) H. E. Zimmerman and R. M. Paufler, THIS JOURNAL, **82**, 1514 (1960), recently have prepared the parent compound, bicyclo[2.2.2]-octa-2,5,7-triene.

(3) A. T. Blomquist and Y. C. Meinwald, THIS JOURNAL, **81**, 667 (1959).