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## Bis-(polyfluoroalkyl)-acetylenes. II. Bicycloöctatrienes Through 1,4-Addition of Bis-(polyfluoroalkyl)-acetylenes to Aromatic Rings<sup>1</sup>

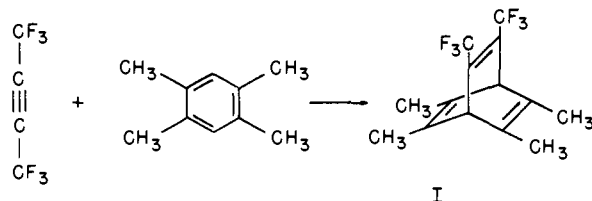
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Bis-(polyfluoroalkyl)-acetylenes add 1,4 to aromatic rings such as those in durene and naphthalene to form bicycloöctatrienes. The reaction of hexafluoro-2-butyne with benzene produces a mixture of trifluoromethylated benzenes and naphthalenes, products probably derived from a bicycloöctatriene formed by 1,4-addition of the butyne to benzene.

Normal Diels-Alder additions of acetylenes to aromatic rings previously have been restricted to very reactive compounds such as anthracene and furan.<sup>2</sup> Certain substituted naphthalenes and, with difficulty, naphthalene itself have given 1,4-adducts with olefinic dienophiles,<sup>3</sup> but apparently no such addition has been accomplished with an acetylene. Diels-Alder additions of olefins to benzene rings have also been reported for specially activated molecules like hydroquinone,<sup>4</sup> but no cases have been found where benzene or a simple derivative of benzene will undergo 1,4-addition of either an olefin or an acetylene.

Bis-(trifluoromethyl)-acetylene has now been found to add 1,4 to durene to provide what we believe to be the first example of a normal Diels-Alder addition to a simply substituted benzenoid ring. This reaction offers a convenient synthesis of the elusive bicycloöctatriene skeleton,<sup>5</sup> since a 40% yield of 2,3,5,6-tetramethyl-7,8-bis-(trifluoromethyl)-bicyclo[2.2.2]octa-2,5,7-triene (I) is readily obtained in one step.



I

As a consequence of its compact structure, I has such high volatility that it is not easily separable from durene by distillation; crystallization of the reaction mixture from aqueous methanol serves as a means of purification. Proof of the symmetrical structure of I is obtainable from the nuclear magnetic resonance spectra. The spectrum for fluorine contains a single sharp band for one kind of trifluoromethyl group, and the proton spectrum contains the expected sharp bands for methyl and tertiary hydrogen in a 6:1 ratio of intensities. The infrared spectrum of I has only one strong absorption in the double bond region ( $5.95 \mu$ ). This absorption probably is due to the tetrasubstituted double

(1) C. G. Krespan, B. C. McKusick and T. L. Cairns, *J. Am. Chem. Soc.*, **82**, 1515 (1960).

(2) H. L. Holmes, "Organic Reactions," Vol. IV, J. Wiley and Sons, Inc., New York, N. Y., 1949, p. 81.

(3) M. C. Kloetzel and H. L. Herzog, *J. Am. Chem. Soc.*, **72**, 1991 (1950).

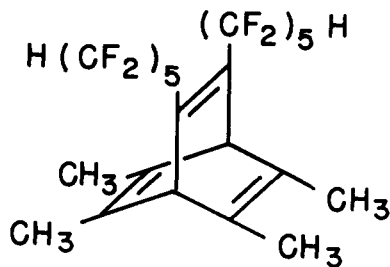
(4) R. E. Cookson and N. S. Wariyar, *Chemistry & Industry*, 915 (1955).

(5) H. E. Zimmerman and R. M. Paufer, *J. Am. Chem. Soc.*, **82**, 1514 (1960), reported the first synthesis of bicyclo[2.2.2]octa-2,5,7-triene.

bond bearing trifluoromethyl groups rather than to those with alkyl groups.<sup>6</sup> The absence of strong interaction between the double bonds in I is indicated by the low intensity bands in its ultraviolet spectrum. A shoulder at  $221 m\mu$  ( $\epsilon$  440) can be accounted for as the lower energy component of a dipolar resonance interaction between the two double bonds bearing methyl groups, but the stabilization energy available from any interactions between the double bonds should be negligible.<sup>1,7</sup>

Further evidence that I is a bicycloöctatriene was obtained by causing a reversal of the Diels-Alder reaction by which such a compound would be formed. Compound I is stable enough to be prepared at  $200^\circ$  but it decomposes at  $250^\circ$  to give durene and 1,2-dimethyl-4,5-bis-(trifluoromethyl)-benzene as the major volatile products. These are the products to be expected from aromatization by loss of hexafluoro-2-butyne and of 2-butyne, respectively. It is interesting to note that bicyclo[2.2.2]octa-2,5,7-triene has thermal stability comparable to I,<sup>5</sup> but that bicyclo[2.2.2]octa-2,5 diene readily loses ethylene to form benzene at  $200^\circ$ .<sup>8</sup>

Diels-Alder addition to durene is evidently a characteristic reaction of bis-(polyfluoroalkyl)-acetylenes, since it was also possible to add 1,1,2-dihydroeicosafuoro-6-dodecyne to durene at  $200^\circ$  to form 2,3,5,6-tetramethyl-7,8-bis-(5-hydrodecafluoropentyl)-bicyclo[2.2.2]octa-2,5,7-triene (II).



II

However, no adduct was detected when durene was treated with acetylene or 1,1,1-trifluoropropyne under similar conditions. These studies demonstrate the great reactivity of bis-(polyfluoroalkyl)-acetylenes as dienophiles. The pronounced electrophilic character of the triple bond, a result of the

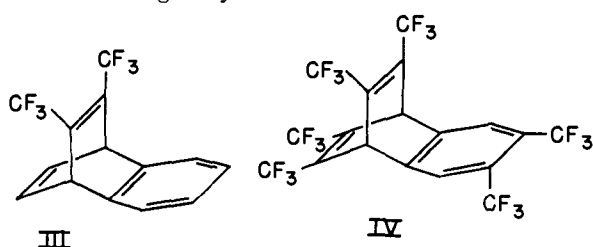
(6) Dr. R. E. Putnam of these laboratories has found double bond absorption at  $5.91 \mu$  in the infrared spectrum of 1,2-bis-(trifluoromethyl)-cyclohexene. The strengths of this band and of the band at  $5.95 \mu$  for I contrast with the very weak bands associated with unfluorinated tetraalkylethylenes.

(7) C. F. Wilcox, Jr., S. Winstein and W. G. McMillan, *J. Am. Chem. Soc.*, **82**, 5450 (1960).

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

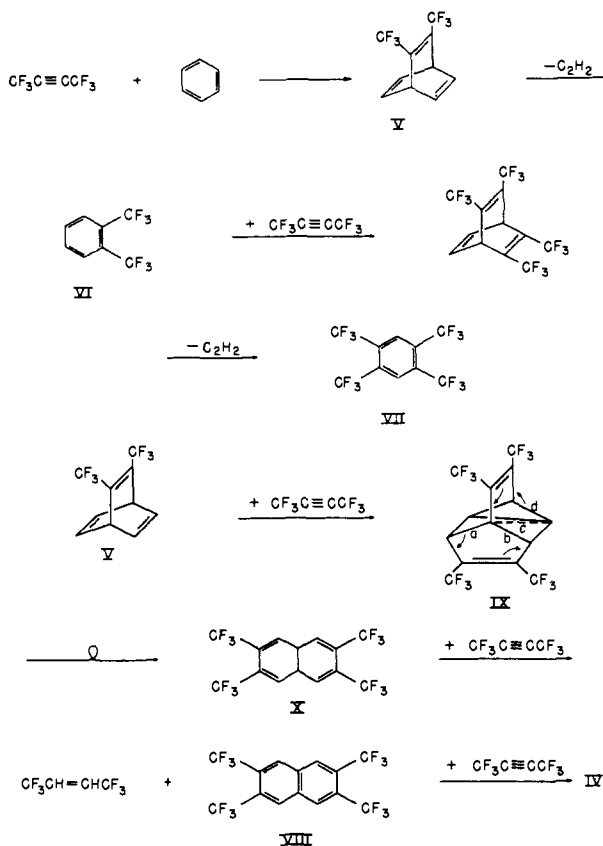
presence of two electronegative fluoroalkyl groups, can be capitalized on in synthetic work because these highly fluorinated acetylenes are thermally stable and resistant to self-condensation.

Hexafluoro-2-butyne was previously found to undergo the Diels-Alder reaction with acyclic 1,3-dienes.<sup>9</sup> Both hexafluoro-2-butyne and 1,6-dichlorooctafluoro-3-hexyne have now been found to add readily to the 9,10-positions of anthracene. Naphthalene also reacts rapidly with hexafluoro-2-butyne at 200° to give a Diels-Alder adduct (III), apparently the first such product to be obtained directly from naphthalene and an acetylene. The susceptibility of the naphthalene nucleus to attack by bis-(polyfluoroalkyl)-acetylenes is demonstrated by the addition of hexafluoro-2-butyne to 2,3,6,7-tetrakis-(trifluoromethyl)-naphthalene. In spite of the low density of electrons in the aromatic ring system caused by the presence of four electron-withdrawing groups, the Diels-Alder adduct IV can be formed in good yield.



Little reaction occurs between benzene and hexafluoro-2-butyne at 200° under pressure, but at 250° reaction occurs readily. Seven products can be isolated from the reaction mixture: 1,1,1,4,4,4-hexafluoro-*cis*-2-butene (6% yield); 1,2-bis-(trifluoromethyl)-benzene, VI (8% yield); 1,2,4-tris-(trifluoromethyl)-benzene (2%); 1,2,4,5-tetrakis-(trifluoromethyl)-benzene, VII (2%); 1,4,6,7-tetrakis-(trifluoromethyl)-naphthalene, XIV (6%); 2,3,6,7-tetrakis-(trifluoromethyl)-naphthalene, VIII (30%); and 2,3,6,7-tetrakis-(trifluoromethyl)-1,4-[1,2-bis-(trifluoromethyl)-etheno]-1,4-dihydronaphthalene, IV (2%). It seems evident that the higher temperature required for a rapid reaction with benzene as opposed to durene is a result of the lower reactivity of benzene as a diene. At the higher temperature, 250°, the bicyclo[2.2.1]hept-2-ene (V) should undergo the reverse Diels-Alder reaction, just as the durene adduct I has been shown to reverse. Thus, the absence of V from the list of products isolated is to be expected, as is the presence of 1,2-bis-(trifluoromethyl)-benzene (VI). Compound VI apparently can react further with hexafluoro-2-butyne by a similar path to form the tetra-substituted benzene VII, although the low reactivity of VI and the presence of an excess of benzene would oppose the formation of appreciable amounts of VII. It may be that the dissociation of V leads first to activated VI, which can interact readily with hexafluoro-2-butyne, or that a direct displacement of acetylene from V can occur. A similar discrepancy is observed in the reaction of benzotrifluoride with hexafluoro-2-butyne at 250°; in this case the reaction is sluggish, as expected, but 1,2,4,5-

tetrakis-(trifluoromethyl)-benzene (VII) is formed in approximately the same yield as the normal products, 1,2-bis-(trifluoromethyl)-benzene and 1,2,4-tris-(trifluoromethyl)-benzene. The formation of the latter compound from benzene does not seem explicable in straightforward terms except as a result of pyrolytic or hydrolytic loss of a trifluoromethyl group from VI or VII.



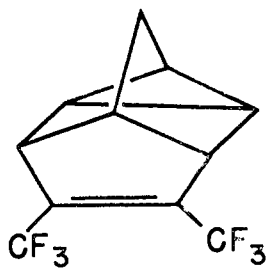
The source of the main product, 2,3,6,7-tetrakis-(trifluoromethyl)-naphthalene (VIII), is a more complex reaction in which the benzene ring undergoes a remarkable rearrangement. A logical way to rationalize the introduction of the required two molecules of hexafluoro-2-butyne into the product is to accept the bicyclo[2.2.1]hept-2-ene V as an intermediate that can not only revert to an aromatic compound by loss of an acetylene, but also can add another molecule of hexafluoro-2-butyne to form the bridged intermediate IX. Analogies to this reaction may be found in the addition of dienophiles such as tetracyanoethylene<sup>10</sup> and maleic anhydride<sup>11</sup> to bicycloheptadiene to give bridged adducts similar to IX, and we have obtained the analogous product XI by addition of hexafluoro-2-butyne to bicycloheptadiene at 150°.

As indicated by the arrows in structure IX, the rearrangement to a dihydronaphthalene with the proper orientation of substituents can be accomplished readily by a migration of electrons. Bonds a and b are presumably the weakest bonds present in IX, since homolytic cleavage of either

(9) R. E. Putnam, R. J. Harder and J. E. Castle, *J. Am. Chem. Soc.*, **83**, 391 (1961).

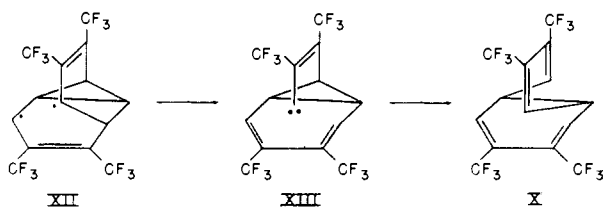
(10) A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **81**, 667 (1959).

(11) E. F. Ullman, *Chemistry & Industry*, 1173 (1958).



XI

leads to a diradical stabilized by interaction of both electrons with double bonds. The diradical XII formed by cleavage of one of these bonds might gain stabilization energy by cleavage of the other bond to give the methylene XIII with the non-bonded electrons still conjugated to a double bond. The methylene carbon could then attack the electrons of the cyclopropane ring,<sup>12</sup> ultimately forming the new bond, c, while breaking bond d. Dehydrogenation of X by hexafluoro-2-butyne to form VIII accounts for the formation of *cis*-1,1,1,4,4,4-hexafluoro-2-butene as a by-product.



Another tetrakis-(trifluoromethyl)-naphthalene formed as a minor product is thought to have the substituents in the 1,4,6,7-positions on the basis of the nuclear magnetic resonance spectra for H<sup>1</sup> and F<sup>19</sup>. The spectrum for fluorine consists of two peaks in 1:1 ratio in fields characteristic of adjacent trifluoromethyl groups for one peak and isolated trifluoromethyl groups for the other. The proton resonances are also two peaks of the same intensity with no splitting detectable, indicating the hydrogen atoms are not on adjacent carbon atoms or are in the same environment. 1,4,6,7-Tetrakis-(trifluoromethyl)-naphthalene (XIV) is the only compound that fits the above requirements.

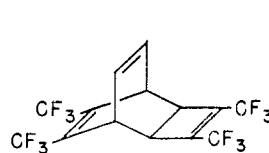
A likely mechanism to account for XIV involves the formation of a cyclobutene ring when either the first or second molecule of hexafluoro-2-butyne is added to benzene. No such thermal reaction has yet been found for hexafluoro-2-butyne,<sup>13</sup> but light-catalyzed reactions of benzene with compounds such as maleic anhydride<sup>14</sup> have been reported to give cyclobutane derivatives. Assuming that the intermediate XV containing a cyclobutane ring is formed, it could pyrolyze to XIV by a series of transformations such as those proposed for the pyrolysis of XVI, the adduct of dimethyl acetylenedicarboxylate with cyclooctatetraene.<sup>15</sup> Several al-

(12) Assuming the electron density around a cyclopropane ring renders it similar to a double bond, a somewhat analogous reaction is the attack of propargylene on olefins reported by P. S. Skell and J. Klebe, *J. Am. Chem. Soc.*, **82**, 247 (1960).

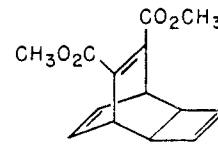
(13) We have observed no reaction of ethylene with hexafluoro-2-butyne at 250° under pressure; at higher temperatures a spectrum of high-boiling oils is produced.

(14) H. J. F. Angus and D. Bryce-Smith, *Proc. Chem. Soc.*, 326 (1959).

ternative rearrangements leading to VIII as well as XIV are possible, but the paths outlined above seem the most probable.



XV



XVI

### Experimental<sup>16</sup>

**2,3,5,6-Tetramethyl-7,8-bis-(trifluoromethyl)-bicyclo[2.2.2]octa-2,5,7-triene (I).**—A mixture of 32 g. (0.20 mole) of hexafluoro-2-butyne and 20.1 g. (0.15 mole) of durene was heated under autogenous pressure at 200° for 10 hours in an 80-ml. slaker tube. Two recrystallizations of the resulting crude solid from methanol containing a small amount of water gave 18.2 g. (41% yield based on durene) of pure 2,3,5,6-tetramethyl-7,8-bis-(trifluoromethyl)-bicyclo[2.2.2]octa-2,5,7-triene, m.p. 56–57°.

*Anal.* Calcd. for C<sub>14</sub>H<sub>14</sub>F<sub>6</sub>: C, 56.76; H, 4.76; F, 38.48; mol. wt., 296. Found: C, 56.75; H, 5.09; F, 38.64; mol. wt., 296 (mass spectrometer).

The infrared spectrum showed only one band for C=C at 5.95 μ (KBr wafer). Absorption in the ultraviolet occurred at λ<sub>max</sub><sup>in octane</sup> 287 mμ (ε 70), shoulder at 223 mμ (ε 440). In carbon tetrachloride, the product exhibited nuclear magnetic resonance peaks for a single CF<sub>3</sub> at -957 c.p.s., a single C-H at +45 c.p.s., and a single CH<sub>3</sub> peak at +176 c.p.s. (proton intensities in a ratio of 1:6).

**Pyrolysis of the Durene-Hexafluoro-2-butyne Adduct.**—Ten grams (0.034 mole) of pure 2,3,5,6-tetramethyl-7,8-bis-(trifluoromethyl)-bicyclo[2.2.2]octa-2,5,7-triene was heated at 250° for 10 hours under autogenous pressure to give 9.0 g. of oil and no gaseous products. Distillation of this oil afforded 3.2 g. of a mixture of oil and a small amount of solid, b.p. 84–91° (20 mm.). The solid was shown to be durene by a melting point of 79–80° that was unchanged by admixture with authentic durene. Analysis of the oil by infrared spectroscopy showed it to be mainly 1,2-dimethyl-4,5-bis-(trifluoromethyl)-benzene,<sup>17</sup> with some durene and a very small amount of starting material also present.

**2,3,5,6-Tetramethyl-7,8-bis-(5-hydrodecafluoropentyl)-bicyclo[2.2.2]octa-2,5,7-triene (II).**—A mixture of 15.2 g. (0.029 mole) of 1,12-dihydroeicosafuoro-6-dodecyne<sup>18</sup> and 6.7 g. (0.05 mole) of durene was heated at 200° for 15 hours in a sealed glass tube. The reaction mixture was stirred with 25 ml. of petroleum ether, cooled and filtered to give 3.9 g. (58%) of recovered crude durene. Distillation of the filtrate gave another 2.2 g. (33%) of recovered durene, 5.8 g. (38%) of recovered dodecyne, b.p. 70–75° (14 mm.), and 1.2 g. (6% yield) of the desired bicyclo-octatriene, b.p. 98–99° (0.2 mm.).

*Anal.* Calcd. for C<sub>22</sub>H<sub>16</sub>F<sub>20</sub>: C, 40.01; H, 2.44; F, 57.55. Found: C, 40.08; H, 2.33; F, 57.47.

The infrared spectrum contained a band for C=C at 6.04 μ. Absorption in the ultraviolet region was composed of weak shoulders in the 230–240 mμ region with a possible weak shoulder at 270 mμ. The nuclear magnetic resonance

(15) M. Avram, C. Nenitzescu and E. Marica, *Chem. Ber.*, **90**, 1857 (1957), heated XVI at 300° to obtain not only dimethyl phthalate, but also dimethyl 2,6-naphthalenedicarboxylate and its dihydro derivative.

(16) All boiling points and melting points are uncorrected. The nuclear magnetic resonance spectra were obtained by means of a high resolution nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates, operating at 56.4 mc./sec. and approximately 14,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the H<sup>1</sup> resonance of water and the F<sup>19</sup> resonance of trifluoroacetic acid. Negative frequency displacements indicate resonances occurring at lower field than the reference.

(17) The authentic sample of this material was supplied by Dr. R. E. Putnam of these laboratories.

(18) C. G. Krespan, R. J. Harder and J. J. Drysdale, *J. Am. Chem. Soc.*, **83**, 3424 (1961).

spectrum contained peaks for a  $\text{CF}_2$  group adjacent to a double bond at +1643 c.p.s.; internal  $\text{CF}_2$  groups at +2348, +2580 and +2987 c.p.s.; and a doublet for terminal  $\text{CF}_2$  group at +3376 and +3432 c.p.s. The proton spectrum consisted of a triplet for the terminal hydrogen centered at -44 c.p.s. with satellites at -97 and +12 c.p.s., tertiary hydrogen at +52 c.p.s., and a  $\text{CH}_3$  peak at +197 c.p.s.

**1,4-Etheno-2,3-bis-(trifluoromethyl)-1,4-dihydronaphthalene (III).**—A mixture of 25.6 g. (0.20 mole) of naphthalene and 24 g. (0.15 mole) of hexafluoro-2-butyne was heated at 225° for 1.5 hours under autogenous pressure in an 80-ml. shaker tube. Distillation gave a mixture of naphthalene and product as forerun, then 16.1 g. (37% yield based on butyne) of colorless oil, b.p. 96° (10 mm.),  $n_D^{25}$  1.4597. The 1,4-etheno-2,3-bis-(trifluoromethyl)-1,4-dihydronaphthalene crystallized on standing to a solid melting at 42–43°.

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_8\text{F}_6$ : C, 57.94; H, 2.78; F, 39.28. Found: C, 58.38; H, 3.06; F, 39.15.

Hydrogenation at 25° over platinum catalyst in ethanol showed the presence of one readily hydrogenated double bond.

Bands for unsaturation occurred at 5.93 and 6.22  $\mu$  in the infrared. Absorption in the ultraviolet occurred at  $\lambda_{\text{max}}^{\text{ethanol}}$  222 m $\mu$  ( $\epsilon$  2,500), 259 m $\mu$  ( $\epsilon$  360), 266 m $\mu$  ( $\epsilon$  370), shoulder at 272 m $\mu$ . The nuclear magnetic resonance spectra contained peaks for  $\text{CF}_2$  at -812 c.p.s., tertiary proton at +12 c.p.s., and unsaturated C-H at -100, -84 and -73 c.p.s. The proton resonances were all of equal intensity and had considerable fine structure.

**2,3,6,7-Tetrakis-(trifluoromethyl)-1,4-[1,2-bis-(trifluoromethyl)-etheno]-1,4-dihydronaphthalene (IV).**<sup>19</sup>—A mixture of 1.55 g. (0.004 mole) of 2,3,6,7-tetrakis-(trifluoromethyl)-naphthalene, 0.81 g. (0.005 mole) of hexafluoro-2-butyne and 2.0 ml. of perfluorodimethylcyclohexane was sealed in a platinum tube under a nitrogen atmosphere. The tube then was pressured externally with 800 atmospheres of nitrogen and heated at 225° for 16 hours. It was cooled to room temperature and opened, and the liquid fraction (2.56 g.) was decanted. The residual white solid was dried to give 1.73 g. (79% yield) of crude product, m.p. 110–117°. Recrystallization of this material from methanol gave pure product, m.p. 122–123° (sealed tube).

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_4\text{F}_{18}$ : C, 38.45; H, 0.72; F, 60.83. Found: C, 38.62; H, 1.18; F, 60.46.

Bands for unsaturation were found at 5.88, 5.96 and 6.26  $\mu$  in the infrared. Absorption in the ultraviolet occurred at  $\lambda_{\text{max}}^{\text{ethanol}}$  270 m $\mu$  ( $\epsilon$  900), 277 m $\mu$  ( $\epsilon$  840), shoulder at 228 m $\mu$ . Nuclear magnetic resonance bands (acetone solution) were found for  $\text{CF}_2$  peaks in 1:2 ratio at -1006 and -853 c.p.s., and C-H peaks in 1:1 ratio at -185 and -62 c.p.s.

**9,10-[1,2-Bis-(trifluoromethyl)-etheno]-9,10-dihydroanthracene.**—A mixture of 17.8 g. (0.10 mole) of anthracene and 24 g. (0.15 mole) of hexafluoro-2-butyne was heated at 200° for 2 hours under autogenous pressure in an 80-ml. shaker tube. Recrystallization of the solid product from 95% ethanol gave 24.2 g. (71% yield) of 9,10-[1,2-bis-(trifluoromethyl)-etheno]-9,10-dihydroanthracene, m.p. 109–110°.

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{10}\text{F}_6$ : C, 63.53; H, 2.96; F, 33.50. Found: C, 63.88; H, 3.09; F, 33.61.

The infrared spectrum contained a strong band for  $\text{C}=\text{C}$  at 5.94  $\mu$  with several weak bands at 5.7–6.75  $\mu$ . Absorption in the ultraviolet occurred at  $\lambda_{\text{max}}^{\text{acetone}}$  270 m $\mu$  ( $\epsilon$  1,010), 277 m $\mu$  ( $\epsilon$  1,240), shoulder at 225 m $\mu$ . The nuclear magnetic resonance spectra (acetone solution) showed a single  $\text{CF}_2$  peak at -923 c.p.s., aromatic hydrogen peaks of equal intensity at -110 and -90 c.p.s., and a tertiary hydrogen peak at -23 c.p.s. with half the intensity of the other proton resonances.

**9,10-[1,2-Bis-(2-chlorotetrafluoroethyl)-etheno]-9,10-dihydroanthracene.**—When 14.8 g. (0.05 mole) of 1,6-dichlorooctafluoro-3-hexyne<sup>18</sup> and 8.9 g. (0.05 mole) of anthracene were heated at 200° for 10 hours under pressure, there was obtained 19 g. of solid. Recrystallization of this material from 95% ethanol gave 15.2 g. (64% yield) of 9,10-[1,2-bis-(2-chlorotetrafluoroethyl)-etheno]-9,10-dihydroanthracene, m.p. 72–74°.

(19) The authors are indebted to Dr. G. N. Sausen of these laboratories for this experiment.

*Anal.* Calcd. for  $\text{C}_{20}\text{H}_{10}\text{Cl}_2\text{F}_8$ : C, 50.76; H, 2.13; Cl, 14.99; F, 32.12. Found: C, 50.80; H, 2.58; Cl, 14.90; F, 32.16.

Infrared bands for unsaturation occurred at 6.07 and 6.27  $\mu$ . Absorption in the ultraviolet came at  $\lambda_{\text{max}}^{\text{acetone}}$  260 m $\mu$  ( $\epsilon$  900), 270 m $\mu$  broad ( $\epsilon$  1,030), 278 m $\mu$  ( $\epsilon$  1,180), shoulder at 225 m $\mu$ .

**Reaction of Hexafluoro-2-butyne with Benzene.**—Eighty-one grams (0.50 mole) of hexafluoro-2-butyne and 200 ml. of benzene were heated in a 400-ml. tube at 250° under autogenous pressure for 12 hours. The liquid reaction mixture, 244 g., gave on distillation a number of products.

The first was 4.9 g. (6% yield) of *cis*-1,1,1,4,4,4-hexafluoro-2-butene, b.p. 34–36°. Identification was made by comparison of the infrared spectrum with that of a known sample.

The next fraction was a mixture of substituted benzenes, b.p. 98–99° (210 mm.), separated by vapor phase chromatography into three components. First to come off the column of silicone oil on firebrick was 1.7 g. (2% yield) of 1,2,4,5-tetrakis-(trifluoromethyl)-benzene (VII), m.p. 72–74°, identified by mixture melting point and comparison of the infrared spectrum with that of an authentic sample.<sup>21</sup> Next was 1.3 g. (2% yield) of 1,2,4-tris-(trifluoromethyl)-benzene, a colorless liquid with  $n_D^{25}$  1.3681, later identified by independent synthesis.

*Anal.* Calcd. for  $\text{C}_6\text{H}_3\text{F}_9$ : C, 38.32; H, 1.07; F, 60.62. Found: C, 38.76; H, 1.31; F, 60.56.

The infrared spectrum contained aromatic bands at 6.08, 6.26 and 6.61  $\mu$ . Nuclear magnetic resonance spectroscopy showed  $\text{CF}_2$  peaks at -937 and -701 c.p.s. in a 2:1 ratio, and aromatic hydrogen peaks at -154 and -150 c.p.s. in a 1:2 ratio.

Last off the column was 8.9 g. (8% yield) of 1,2-bis-(trifluoromethyl)-benzene (VI),  $n_D^{25}$  1.3917,<sup>22</sup> identified by infrared spectroscopy.

The final product to distil was 1,4,6,7-tetrakis-(trifluoromethyl)-naphthalene (XIV), b.p. 122–125° (50 mm.). Recrystallization from methanol gave 5.6 g. (6% yield) of crystals, m.p. 102–103°.

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_4\text{F}_{12}$ : C, 42.02; H, 1.01; F, 56.97; mol. wt., 400. Found: C, 42.14; H, 1.15; F, 56.96; mol. wt., 372 (f.p. benzene).

Infrared bands for unsaturation occurred at 6.12 and 6.65  $\mu$  (KBr wafer). Typical naphthalenic absorption in the ultraviolet occurred at  $\lambda_{\text{max}}^{\text{acetone}}$  221 m $\mu$  ( $\epsilon$  107,000), 272 m $\mu$  ( $\epsilon$  6,000), 306 m $\mu$  ( $\epsilon$  640), 319 m $\mu$  ( $\epsilon$  720), shoulders at 265, 282 and 311 m $\mu$ . Nuclear magnetic resonance showed  $\text{CF}_2$  peaks of equal intensity at -991 and -788 c.p.s., and aromatic hydrogen peaks of equal intensity at -186 and -162 c.p.s. (acetone solution). No fine structure could be detected in these peaks.

For reference purposes, the  $\text{H}^1$  and  $\text{F}^{19}$  spectra of three trifluoromethylated benzenes were calibrated. Benzotrifluoride was found to have a  $\text{CF}_2$  band at -812 c.p.s., and proton peaks at -106 (small) and -96 c.p.s. (large), with considerable splitting of the proton peaks. 1,2-Bis-(trifluoromethyl)-benzene had a band at -983 c.p.s. for  $\text{CF}_2$ , and aromatic hydrogen peaks at -126 and -120 c.p.s. (1:1 ratio with fine structure evident). 1,2,4,5-Tetrakis-(trifluoromethyl)-benzene in acetone solution gave a  $\text{CF}_2$  resonance at -958 c.p.s. and a proton resonance at -175 c.p.s. The results coupled with the nuclear magnetic resonance spectra of the product above indicate that trifluoromethyl groups in the product are in the 1,4,6,7-positions (see Discussion).

Two recrystallizations of the distillation residue from methanol gave 29.7 g. (30% yield based on two moles of butyne required per mole of product) of 2,3,6,7-tetrakis-(trifluoromethyl)-naphthalene (VIII), m.p. 173–174° (subl.).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_4\text{F}_{12}$ : C, 42.02; H, 1.01; F, 56.97. Found: C, 42.23; H, 1.44; F, 56.39.

(20) J. H. Simons, "Fluorine Chemistry," Vol. II, Academic Press, Inc., New York, N. Y., 1954, p. 276, reports b.p. 33° for this compound.

(21) Prepared from sulfur tetrafluoride and pyromellitic acid as described by W. R. Hasek, W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

(22) J. H. Simons, "Fluorine Chemistry," Vol. II, Academic Press, Inc., New York, N. Y., 1954, p. 424, reports  $n_D^{25}$  1.3916 for 1,2-bis-(trifluoromethyl)-benzene.

Infrared analysis revealed no strong bands in the 5.8–6.5  $\mu$  region (KBr), but a broad band at *ca.* 6.6  $\mu$ . The Raman spectrum (15 g. in 32 ml. of acetone; illuminated with the 4,358 Å. band of Hg) contained bands at 3.33(w), 6.10(m), 6.37(m), 6.87(s), 7.28(s) and 13.52(m)  $\mu$ . None of these bands occurs in the infrared. Absorption in the ultraviolet occurred at  $\lambda_{\text{max}}^{\text{ethanol}}$  222 m $\mu$  ( $\epsilon$  78,000), 260 m $\mu$  ( $\epsilon$  4,030), 269 m $\mu$  ( $\epsilon$  4,130), 308 m $\mu$  ( $\epsilon$  1,520), 323 m $\mu$  ( $\epsilon$  2,580), 5 other bands in 250–315 m $\mu$  region. A saturated solution in acetone gave nuclear magnetic resonance bands at  $-202$  c.p.s. for aromatic hydrogen and at  $-1005$  c.p.s. for  $\text{CF}_3$ . The structure of this product has been proved by an independent synthesis.

The filtrates from recrystallization of the major product were concentrated and cooled to  $0^\circ$ . The precipitate so obtained was dried and sublimed slowly at  $100^\circ$  (1 atm.). The resulting sublimate was recrystallized twice from methanol to give 1.9 g. (2% yield) of 2,3,6,7-tetrakis-(trifluoromethyl)-1,4-[1,2-bis-(trifluoromethyl)-etheno]-1,4-dihydronaphthalene (IV), m.p.  $122\text{--}123^\circ$  (sealed tube), not depressed when mixed with an authentic sample. Comparison of the infrared spectra of this product and of an authentic sample showed the materials to be the same.

**Independent Synthesis of 2,3,6,7-Tetrakis-(trifluoromethyl)-naphthalene (VIII).**—A sample of 2,3,6,7-naphthalenetetracarboxylic acid was prepared by the reaction of allene with maleic anhydride to give  $\Delta^{9,10}$ -octahydro-2,3,6,7-naphthalenetetracarboxylic acid dianhydride<sup>23</sup> which was dehydrogenated with bromine and hydrolyzed to the tetracid.<sup>24</sup> Reaction of 15.2 g. (0.05 mole) of this tetracarboxylic acid with 130 g. (1.2 moles) of sulfur tetrafluoride was carried out at  $150^\circ$  for 8 hours under pressure.<sup>25</sup> The solid product was stirred with 5% sodium bicarbonate, washed with water, and recrystallized twice from 95% ethanol to give 5.2 g. (26% yield) of 2,3,6,7-tetrakis-

(trifluoromethyl)-naphthalene, m.p.  $174\text{--}175^\circ$  (subl.). Mixed melting point and comparison of infrared spectra showed this product to be identical with the major product obtained from reaction of benzene with hexafluoro-2-butyne.

**Independent Synthesis of 1,2,4-Tris-(trifluoromethyl)-benzene.**—A mixture of 38.4 g. (0.20 mole) of trimellitic anhydride and 194 g. (1.8 moles) of sulfur tetrafluoride was heated in a 400-ml. tube lined with Hastelloy under autogenous pressure at  $200^\circ$  for 2 hours, then at  $300^\circ$  for 4 hours, and finally at  $350^\circ$  for 8 hours.<sup>25</sup> The crude product was washed with 1 liter of 5% sodium bicarbonate, dried, filtered and distilled to give 32.2 g. (57% yield) of 1,2,4-tris-(trifluoromethyl)-benzene, b.p.  $79\text{--}80^\circ$  (100 mm.),  $n_D^{25}$  1.3679. Comparison of the nuclear magnetic resonance and infrared spectra showed this compound to be identical with the tris-(trifluoromethyl)-benzene from hexafluoro-2-butyne and benzene.<sup>25</sup>

**6,7-Bis-(trifluoromethyl)-tetracyclo[3.2.1.1<sup>3,5</sup>.0<sup>2,4</sup>]-non-6-ene (XI).**—A mixture of 18.4 g. (0.20 mole) of bicycloheptadiene, 32 g. (0.20 mole) of hexafluoro-2-butyne and 50 ml. of pentane was heated at  $150^\circ$  for 6 hours under pressure. Distillation of the crude product gave 39.6 g. (78% yield) of an oil, b.p.  $79^\circ$  (30 mm.),  $n_D^{25}$  1.3990, shown by vapor phase chromatography to be a single compound.

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_8\text{F}_6$ : C, 51.98; H, 3.17; F, 44.85. Found: C, 51.80; H, 3.47; F, 44.96.

The infrared spectrum contained a strong band (6.0  $\mu$ ) in the double bond region and C–H absorption at 3.25 (cyclopropyl), 3.32, 3.37 and 3.45  $\mu$ . Nuclear magnetic resonance showed only one kind of trifluoromethyl group to be present; the proton spectrum contained no resonance at low enough field to be attributed to hydrogen on doubly bonded carbon, but was not otherwise interpretable.

(23) K. Alder and O. Ackermann, *Chem. Ber.*, **87**, 1567 (1954).

(24) O. W. Webster, U. S. Patent 2,912,442 (1959).

(25) General procedure described by W. R. Hasek, W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

(26) J. H. Simons, "Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 513, records a previous preparation of 1,2,4-tris-(trifluoromethyl)-benzene, for which only b.p.  $140\text{--}143^\circ$  is reported.

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### Bis-(polyfluoroalkyl)-acetylenes. III. Fluorinated Diphospha- and Diarsabicycloöctatrienes<sup>1</sup>

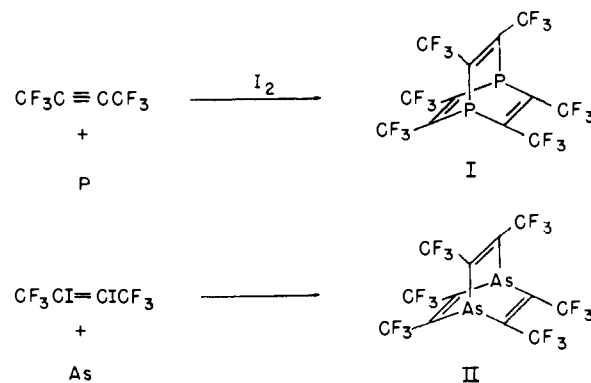
By C. G. KRESPAN

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Hexakis-(trifluoromethyl)-1,4-diphosphabicyclo[2.2.2]octa-2,5,7-triene, a representative of a new heterocyclic system, has been synthesized in one step from elemental phosphorus and hexafluoro-2-butyne. The corresponding diarsabicycloöctatriene has been obtained by reaction of arsenic with the diiodide of hexafluoro-2-butyne.

Benzobicycloöctatrienes such as triptycene<sup>2</sup> have been known for some time, but carbocyclic compounds containing the isolated bicycloöctatriene skeleton have only recently been synthesized.<sup>3,4</sup> Similarly, the analog of triptycene with arsenic atoms at the bridgehead positions has been reported,<sup>5</sup> but no heterocyclic compound containing the isolated bicycloöctatriene skeleton has been prepared.

It has now been found possible to prepare 2,3,5,6,7,8-hexakis-(trifluoromethyl)-1,4-diphosphabicyclo[2.2.2]octa-2,5,7-triene (I) in one step from hexa-



(1) C. G. Krespan, B. C. McKusick and T. L. Cairns, *J. Am. Chem. Soc.*, **82**, 1515 (1960).

(2) P. D. Bartlett, M. J. Ryan and S. G. Cohen, *ibid.*, **64**, 2649 (1942).

(3) H. E. Zimmerman and R. M. Paufer, *ibid.*, **82**, 1514 (1960).

(4) C. G. Krespan, B. C. McKusick and T. L. Cairns, *ibid.*, **83**, 3428 (1961).

(5) E. Krause and A. von Grosse, "Die Chemie der metallorganischen Verbindungen," Borntraeger, Berlin, 1937, p. 572.

fluoro-2-butyne. The reaction is conveniently carried out by heating red phosphorus with hexafluoro-2-butyne and a catalytic amount of iodine at  $200^\circ$  under pressure. The colorless, very volatile solid