

Infrared analysis revealed no strong bands in the 5.8–6.5 μ region (KBr), but a broad band at *ca.* 6.6 μ . 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) μ . None of these bands occurs in the infrared. Absorption in the ultraviolet occurred at $\lambda_{\text{max}}^{\text{ethanol}}$ 222 m μ (ϵ 78,000), 260 m μ (ϵ 4,030), 269 m μ (ϵ 4,130), 308 m μ (ϵ 1,520), 323 m μ (ϵ 2,580), 5 other bands in 250–315 m μ 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 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° . The precipitate so obtained was dried and sublimed slowly at 100° (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 dianhydride²³ which was dehydrogenated with bromine and hydrolyzed to the tetraacid.²⁴ Reaction of 15.2 g. (0.05 mole) of this tetra-carboxylic acid with 130 g. (1.2 moles) of sulfur tetrafluoride was carried out at 150° for 8 hours under pressure.²⁵ 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° for 2 hours, then at 300° for 4 hours, and finally at 350° for 8 hours.²⁵ 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.²⁵

6,7-Bis-(trifluoromethyl)-tetracyclo[3.2.1.1^{3,8}.0^{2,4}]-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° for 6 hours under pressure. Distillation of the crude product gave 39.6 g. (78% yield) of an oil, b.p. 79° (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 μ) in the double bond region and C–H absorption at 3.25 (cyclopropyl), 3.32, 3.37 and 3.45 μ . 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 Diphospho- and Diarsabicyclooctatrienes¹

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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 diarsabicyclooctatriene has been obtained by reaction of arsenic with the diiodide of hexafluoro-2-butyne.

Benzobicyclooctatrienes such as triptycene² have been known for some time, but carbocyclic compounds containing the isolated bicyclooctatriene skeleton have only recently been synthesized.^{3,4} Similarly, the analog of triptycene with arsenic atoms at the bridgehead positions has been reported,⁵ but no heterocyclic compound containing the isolated bicyclooctatriene 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-

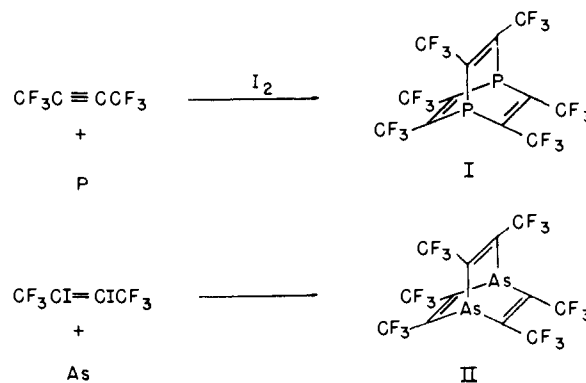
(1) C. G. Krespan, B. C. McKusick and T. L. Cairns, *J. Am. Chem. Soc.*, **82**, 1515 (1960).

(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° under pressure. The colorless, very volatile solid

is easily isolated in 43% yield. Formation of the analogous diarsine II was accomplished by a similar reaction of elemental arsenic with the diiodide of hexafluoro-2-butyne.

The proof of structure for I rests largely on physical evidence. Analyses show that a molecule of I contains two atoms of phosphorus and three molecules of hexafluoro-2-butyne. Absorption in the double bond region of the infrared (6.22 μ) occurs at longer wave length than for similar carbocyclic compounds,^{3,4} indicating direct attachment of phosphorus to the doubly bonded carbon atoms. Similarly, the ultraviolet absorption is enhanced and a longer wave length than for bicyclo-octatrienes containing no heteroatoms.^{3,4} The high volatility of I fits a symmetrical structure, and such a structure is in accord with the nuclear magnetic resonance spectrum for F¹⁹. This spectrum contains only a doublet arising from the resonance of one kind of trifluoromethyl group split by adjacent phosphorus.

The presence of two phosphine groups per molecule of I is shown by the formation of a solid complex with one mole of diborane at low temperature.⁶ This adduct is unstable, decomposing into its components at room temperature. Compound I is insoluble in concentrated sulfuric acid, and is unreactive toward atmospheric oxygen, methyl iodide at room temperature, benzyl chloride at 100°, or bromine dissolved in chloroform. The lack of reactivity toward large entering groups may be partly a result of steric hindrance by the trifluoromethyl groups to attack on the neighboring phosphorus atom. However, the phosphorus atoms in I are subject to inductive withdrawal of electrons by the vinyl groups, and this effect is intensified by the highly electronegative trifluoromethyl groups, which render the phosphorus atom much less basic than usual.^{7,8} The phosphorus atoms in I might also be involved in resonance with the attached vinyl groups, since it is possible for overlap of the $d\pi-p\pi$ orbitals to occur, even in this non-planar system.⁹

Evidence similar to that outlined above points to the diarsine II as the structure of the volatile product formed from arsenic and 2,3-diiodohexafluoro-2-butene.

(6) The author is indebted to Dr. G. W. Parshall of these laboratories for this experiment.

(7) Compound I may, in a sense, be looked on as a vinylog of tris(trifluoromethyl)-phosphine, which R. N. Haszeldine and B. O. West, *J. Chem. Soc.*, 3631 (1956), report does not form isolable phosphonium salts.

(8) W. A. Henderson, Jr., and C. A. Streuli, *J. Am. Chem. Soc.*, **82**, 5791 (1960).

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Experimental¹⁰

2,3,5,6,7,8-Hexakis-(trifluoromethyl)-1,4-diphosphabicyclo[2.2.2]octa-2,5,7-triene.—A reaction of 12.4 g. (0.40 gram-atom) of red phosphorus and 32 g. (0.20 mole) of hexafluoro-2-butyne with a catalytic amount of iodine (2.5 g., 0.01 mole) was carried out at 200° for 8 hours under autogenous pressure. The reaction mixture was heated a short time at 90° (10 mm.) to remove volatile oils. The solid residue then was shaken with mercury and sublimed at 100° (10 mm.) to give 22.4 g. of a volatile solid. Recrystallization of this solid from acetic acid followed by another sublimation at 100° (100 mm.) gave 16.2 g. (43% yield based on the butyne) of 2,3,5,6,7,8-hexakis-(trifluoromethyl)-1,4-diphosphabicyclo[2.2.2]octa-2,5,7-triene, m.p. 118–119° (subl.).

Anal. Calcd. for C₁₂F₁₈P₂: C, 26.30; F, 62.40; P, 11.31; mol. wt., 548. Found: C, 27.04; F, 62.35; P, 11.48; mol. wt., 548 (mass spectrometer).

The ultraviolet spectrum showed absorption at $\lambda_{\text{max}}^{\text{acetone}} 262 \text{ m}\mu$ (ϵ 450), 316 m μ (ϵ 640). Absorption in the double bond region of the infrared occurred at 6.22 μ (KBr wafer). The nuclear magnetic resonance spectrum in dimethylformamide solution consisted of a doublet for CF₃ at –1210 and –1170 c.p.s. Splitting of these peaks was the same at 40 megacycles, indicating the presence of a single kind of CF₃ split by nearby phosphorus.

This compound also was prepared in good yield by reaction of red phosphorus with 2,3-diiodohexafluoro-2-butene at 210° under pressure.

2,3-Diiodohexafluoro-2-butene.—Reaction of 263 g. (1.6 moles) of hexafluoro-2-butyne with 437 g. (1.7 moles) of iodine at 200° for 3 hours under autogenous pressure gave 665 g. of crude product. This was shaken with mercury, filtered and distilled to give 486 g. (72% yield) of 2,3-diiodohexafluoro-2-butene, b.p. 77–78° (50 mm.). Nuclear magnetic resonance spectroscopy showed both the *cis* and *trans* isomers to be present.

Anal. Calcd. for C₄F₈I₂: C, 11.55; F, 27.41; I, 61.03. Found: C, 11.85; F, 27.17; I, 60.41.

2,3,5,6,7,8-Hexakis-(trifluoromethyl)-1,4-diarsabicyclo[2.2.2]octa-2,5,7-triene.—A mixture of 83.2 g. (0.20 mole) of 2,3-diiodohexafluoro-2-butene and 30.0 g. (0.40 gram-atom) of arsenic was heated at 200° for 10 hours under autogenous pressure. Sublimation of the product at 120° under one atmosphere of nitrogen gave 31.2 g. of volatile solid. Treatment of this solid with mercury, resublimation, and recrystallization from benzene gave 18.6 g. (44% yield based on the diiodide) of colorless 2,3,5,6,7,8-hexakis-(trifluoromethyl)-1,4-diarsabicyclo[2.2.2]octa-2,5,7-triene, m.p. 139–140° (subl.). An analytical sample was obtained by recrystallization from acetic acid.

Anal. Calcd. for C₁₂F₁₈As₂: C, 22.66; F, 53.78; As, 23.56. Found: C, 22.90; F, 53.87; As, 24.44.

The infrared spectrum contained absorption in the double bond region at 6.19 μ (KBr wafer). Absorption in the ultraviolet occurred at $\lambda_{\text{max}}^{\text{acetone}} 297 \text{ m}\mu$ (ϵ 960) with a shoulder at 238 m μ (ϵ 900). The nuclear magnetic resonance spectrum consisted of a single peak for CF₃ at –1325 c.p.s. (dimethylformamide solution).

(10) Melting and boiling points are uncorrected. Nuclear magnetic resonance spectra were obtained from 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 F¹⁹ resonance of trifluoroacetic acid. Negative frequency displacements are for resonances occurring at lower field than the reference.