

under reflux for 2.5 hours. After cooling and adding 150 ml. of water, the product was isolated in the same manner as III and distilled through a 20 × 1-cm. column packed with glass helices. The recovery of cycloöctatetraene was 18.5 g. (24%), b.p. 62.5° (68 mm.), and the yield of crude *s*-butylcycloöctatriene was 14.7 g., b.p. 67–80° (5 mm.). Redistillation through a semi-micro column yielded 11.2 g. (32%) of IX, b.p. 58.5–60° (1.8 mm.), n_D^{25} 1.4947, d_4^{25} 0.8879, λ_{max} 270 m μ , ϵ_{max} 1740 (in cyclohexane, Fig. 1).

Anal. Calcd. for C₁₂H₁₈: C, 88.82; H, 11.18. Found: C, 88.99; H, 11.25.

Hydrogenation of a solution of 2.0 g. of IX in 25 ml. of acetic acid in the presence of 0.46 g. of platinum oxide was complete in 36 minutes and required 91.3% of three molar equivalents of hydrogen. The reduction product amounted to 1.39 g. of *s*-butylcycloöctane, b.p. 61–62° (1 mm.), n_D^{25} 1.4630, with an infrared spectrum identical with that of an authentic sample described below.

Anal. Calcd. for C₁₂H₂₄: C, 85.64; H, 14.36. Found: C, 85.54; H, 14.07.

1-*s*-Butylcycloöctanol.—A solution of 6.96 g. of cycloöctanone in 25 ml. of pentane was added during 30 minutes with stirring to the *s*-butyllithium prepared from 27.8 g. of *s*-butyl chloride and 4.16 g. of lithium wire in 380 ml. of olefin-free pentane (0.138 mole of *s*-butyllithium was present according to acidimetric titration of an aliquot). The mixture was heated under reflux for 2.5 hours, cooled, and iced ammonium chloride was added. The pentane layer was

combined with four 50-ml. pentane extracts of the aqueous layer, washed with water, dried over magnesium sulfate, and concentrated. Distillation through a semi-micro column yielded 5.1 g. of crude 1-*s*-butylcycloöctanol, b.p. 126–130° (15 mm.), and redistillation gave 3.3 g., b.p. 98–99° (1.3 mm.), n_D^{25} 1.4840, d_4^{25} 0.9462.

Anal. Calcd. for C₁₂H₂₄O: C, 78.09; H, 13.13. Found: C, 78.27; H, 13.40.

***s*-Butylcycloöctene (IX).**—A solution of 3.3 g. of 1-*s*-butylcycloöctanol and 60 mg. of iodine in 30 ml. of toluene was heated under reflux for 18 hours, while the water formed was removed with a Dean and Stark separator. The solution was cooled, washed with 5% sodium thiosulfate solution and with water, and dried over sodium sulfate. Fractionation through a semi-micro column yielded 2.74 g. of IX, b.p. 82.5–83.5° (10 mm.), n_D^{25} 1.4725–1.4755. An analytical sample had b.p. 83.5° (10 mm.), n_D^{25} 1.4739.

Anal. Calcd. for C₁₂H₂₂: C, 86.66; H, 13.34. Found: C, 86.52; H, 13.20.

***s*-Butylcycloöctane (X).**—A solution of 2.02 g. of IX in 25 ml. of acetic acid was reduced in 65 minutes in the presence of 0.5 g. of prerduced platinum oxide and absorbed 101% of one molar equivalent of hydrogen. The product amounted to 1.38 g. of *s*-butylcycloöctane, b.p. 86° (8 mm.), n_D^{25} 1.4629.

Anal. Calcd. for C₁₂H₂₄: C, 85.64; H, 14.36. Found: C, 85.68; H, 14.38.

CAMBRIDGE, MASSACHUSETTS

RECEIVED JULY 9, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Cyclic Polyolefins. XXII. Substituted Cycloöctatetraenes from Substituted Acetylenes¹

BY ARTHUR C. COPE AND HUGH C. CAMPBELL

Copolymerization of mono- and 1,2-disubstituted acetylenes with acetylene has been found to provide a direct synthesis of mono- and 1,2-disubstituted cycloöctatetraenes. Substituted benzenes are formed as minor by-products by combination of the reactants in a 1:2 ratio. Methylcycloöctatetraene, *n*-propylcycloöctatetraene, *n*-butylcycloöctatetraene, phenylcycloöctatetraene and 1,2-dimethylcycloöctatetraene have been prepared by this method. The monosubstituted cycloöctatetraenes were identified by quantitative reduction to cycloöctane derivatives or by direct comparison with authentic samples, while 1,2-dimethylcycloöctatetraene was characterized by reduction to 1,2-dimethylcycloöctene, which was converted to decane-2,9-dione by ozonization.

We have reported in a recent communication² that the copolymerization of substituted acetylenes with acetylene under conditions similar to those used for the polymerization of acetylene to cycloöctatetraene³ results in the formation of substituted cycloöctatetraenes by combination of the reactants in a 1:3 ratio. Substituted benzenes also are formed in small amounts under these conditions from the substituted acetylene and acetylene (1:2 ratio), together with benzene and cycloöctatetraene from the polymerization of acetylene. Apparently copolymerizations of this type have not been reported previously. Although reference has been made (ref. 3, p. 37) to the possibility of polymerizing substituted acetylenes to substituted cycloöctatetraenes, it has been reported that phenylacetylene fails to polymerize, and that vinylacetylene yields a gel-like (rather than a cyclic) polymer.⁴

The copolymerizations were conducted according

(1) Supported in part by the Office of Naval Research under Contract N5ori-07822, Project Designation NR-055-96. Presented at the Twelfth National Organic Chemistry Symposium, Denver, Colorado, June 14, 1951.

(2) A. C. Cope and H. C. Campbell, *THIS JOURNAL*, **73**, 3536 (1951).

(3) W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

(4) K. Kammermeyer, "Polymerization of Acetylene to Cycloöctatetraene," Hobart Publishing Co., Washington, D. C., p. 2 (based upon work of the group headed by Reppe).

to a procedure previously described for the polymerization of acetylene to cycloöctatetraene,⁵ by heating a mixture of a substituted acetylene, tetrahydrofuran solvent, nickel acetylacetonate or nickel cyanide catalyst and powdered calcium carbide in a stirred autoclave at 70–90° with acetylene at 300–150 p.s.i. The substituted cycloöctatetraenes were isolated either by fractional distillation of a steam distillate of the reaction mixture, or by benzene extraction of the organic portion of the residue from the steam distillation (or from both of these fractions), according to their volatilities. The substituted cycloöctatetraenes were purified conveniently through crystalline or water-soluble complexes with silver nitrate, from which the hydrocarbons were regenerated by treatment with ammonium hydroxide.

Phenylcycloöctatetraene (I, 17%) and *n*-butylcycloöctatetraene (II, 16%) were obtained by the copolymerization of phenylacetylene and 1-hexyne, respectively, with acetylene. These hydrocarbons had been prepared previously by the reaction of cycloöctatetraene with phenyllithium and *n*-butyllithium,⁶ and were identified by direct comparison

(5) A. C. Cope and L. L. Estes, Jr., *THIS JOURNAL*, **72**, 1129 (1950).

(6) (a) A. C. Cope and M. R. Kinter, *ibid.*, **72**, 630 (1950); **73**, 3424 (1951); (b) A. C. Cope and H. O. Van Orden, *ibid.*, **73**, 175 (1951).

with samples prepared by that route. Preliminary attempts to prepare methylcyclooctatetraene (III) from cyclooctatetraene and methyl lithium had been unsuccessful,^{6b} but III was obtained without difficulty in 16% yield by copolymerization of propyne with acetylene. Methylcyclooctatetraene was isolated as a yellow liquid with an ultraviolet spectrum (Fig. 1) similar to cyclooctatetraene. It was characterized by the infrared spectrum (Fig. 2),

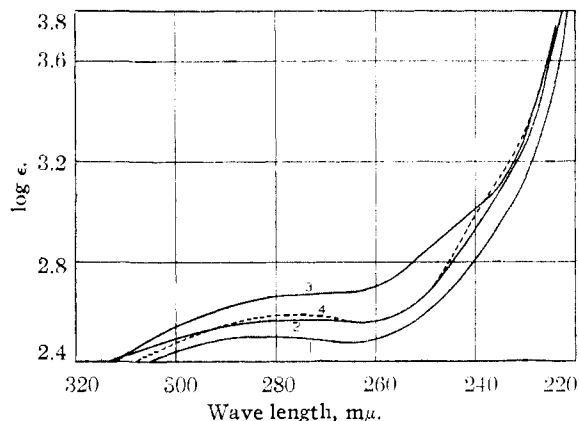


Fig. 1.—Ultraviolet absorption spectra: curve 1, methylcyclooctatetraene (III); curve 2, *n*-propylcyclooctatetraene (V); curve 3, 1,2-dimethylcyclooctatetraene (VII); curve 4, mixture of dimethylcyclooctatetraenes obtained from higher boiling fractions from methylcyclooctatetraene preparations, all in cyclohexane.

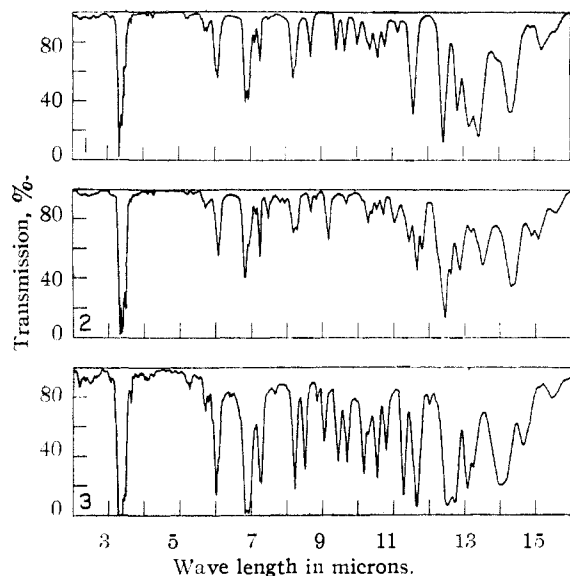


Fig. 2.—Infrared absorption spectra: curve 1, methylcyclooctatetraene (III); curve 2, *n*-propylcyclooctatetraene (V); curve 3, 1,2-dimethylcyclooctatetraene. The spectra were determined without solvent in a 0.025 mm. cell.

preparation of a crystalline maleic anhydride adduct and 2:3 complex with silver nitrate, and by quantitative reduction with the absorption of 97% of four molar equivalents of hydrogen forming methylcyclooctane (IV), identical in infrared absorption spectrum with an authentic sample (Fig. 3). *n*-Propylcyclooctatetraene (V) was prepared similarly from 1-pentyne in 25% yield, and char-

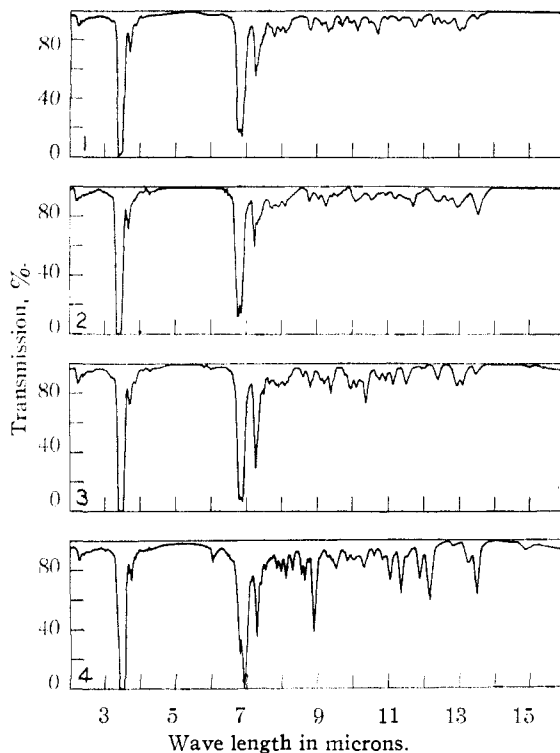
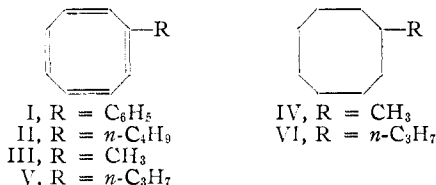


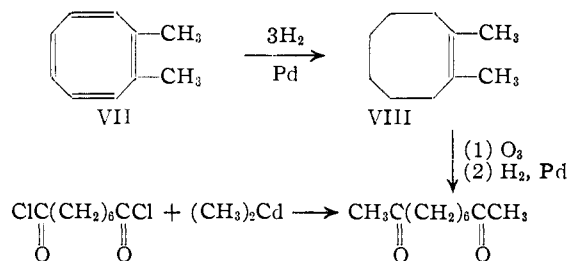
Fig. 3.—Infrared absorption spectra: curve 1, methylcyclooctane (IV); curve 2, *n*-propylcyclooctane (VI); curve 3, 1,2-dimethylcyclooctane; curve 4, 1,2-dimethylcyclooctene (VIII). The spectra were determined without solvent in a 0.025-mm. cell.

acterized by its ultraviolet (Fig. 1) and infrared absorption spectra (Fig. 2), by preparation of a crystalline 1:2 complex with silver nitrate, and by a quantitative hydrogenation in which 100% of four molar equivalents of hydrogen was absorbed and *n*-propylcyclooctane (VI) was formed. Toluene and *n*-propylbenzene were isolated in small amounts in the copolymerizations leading to III and V, respectively.



It was of interest to determine whether combination of two or more molecules of a substituted acetylene with acetylene would occur, forming poly-substituted cyclooctatetraenes. The higher boiling fractions from the copolymerization of propyne with acetylene were examined carefully as a favorable case for the isolation of such products, and yielded a small amount of a yellow mixture of isomeric dimethylcyclooctatetraenes. Evidence supporting this assignment of structure to the mixture was an analysis in agreement with the formula C₁₀H₁₂, color, ultraviolet absorption similar to 1,2-dimethylcyclooctatetraene (Fig. 1), solubility in aqueous silver nitrate, and quantitative reduction with the absorption of 100% of four molar equivalents of hydrogen.

Copolymerization of 2-butyne with acetylene yielded 19% of 1,2-dimethylcyclooctatetraene (VII) as a yellow liquid that was characterized by absorption spectra (Figs. 1 and 2) and preparation of a crystalline maleic anhydride adduct and 1:2 complex with silver nitrate. Confirmation of the structure of VII by reduction to 1,2-dimethylcyclooctane seemed likely to present difficulties, for a mixture of *cis*- and *trans*-forms might result, and independent syntheses of 1,2-dimethylcyclooctane could lead to mixtures of the two forms in a different proportion. A simpler proof of structure of VII became possible through its selective catalytic reduction in the presence of 1% palladium-on-calcium carbonate, with the absorption of 102% of three molar equivalents of hydrogen, forming 1,2-dimethylcyclooctene (VIII). The infrared absorption spectrum of VIII (Fig. 3) contained little if any evidence of absorption due to olefinic C-H in the 3μ region, indicating that the product was fairly homogeneous and had structure VIII. Ozonization of VIII followed by reductive cleavage of the ozonide formed crystalline decane-2,9-dione, identified by comparison of its melting point and the melting point of its dioxime with authentic samples, thus confirming the structure of VIII and VII.



Under the conditions used for copolymerization of substituted acetylenes with acetylene the polymerization of acetylene to cyclooctatetraene is a rapid and convenient process,⁵ but leads to yields of cyclooctatetraene of approximately 25–30%, primarily because of the relatively large amounts of cuprene and benzene formed as by-products. The yields of substituted cyclooctatetraenes obtained (16–25%) are reasonably good considering the cyclooctatetraene yields obtainable under the same conditions, and presumably would be higher under conditions leading to a higher yield of cyclooctatetraene from acetylene. It can be inferred from the large amount of cyclooctatetraene formed from acetylene during the copolymerizations, and from the very small amount of dimethylcyclooctatetraene isomers formed from propyne, that the substituted acetylenes associate somewhat less readily with the catalyst (presumably an electrophilic nickel complex) than does acetylene. The observation that 2-butyne enters readily into the copolymerization establishes the fact that in that case the association with the catalyst is through an electron pair of the triple bond, and by analogy supports the assumption that acetylene itself is associated with the catalyst in a similar manner in the polymerization forming cyclooctatetraene.

Investigation of the preparation of substituted cyclooctatetraenes by the copolymerization of acet-

ylene with substituted acetylenes, including derivatives containing various functional groups, is being continued.

Experimental⁷

Copolymerization Procedure.—In a 1-l. stainless steel stirred autoclave were placed 200–250 g. of dry tetrahydrofuran, 20–50 g. of a substituted acetylene, 10 g. of nickel acetylacetonate and 20 g. of powdered calcium carbide. The air in the system was displaced with acetylene, and the mixture was stirred and heated at 70–90° for 7 to 12 hours at a pressure of 300–150 p.s.i. maintained by repressuring with acetylene at frequent intervals, according to the procedure previously employed for polymerization of acetylene to cyclooctatetraene.⁵ The mixture was steam distilled until 2 l. of distillate was collected to separate volatile material (tetrahydrofuran, benzene, cyclooctatetraene, a substituted benzene and all or part of the substituted cyclooctatetraene, depending upon its volatility) from a water-insoluble residue (largely cuprene from polymerization of acetylene). The water-insoluble portion of the residue was separated by filtration, and extracted in a Soxhlet apparatus for 24 hours with benzene containing a small amount of hydroquinone as a polymerization inhibitor. The benzene extract was concentrated and distilled, and the crude distillate was combined with the residue obtained by fractionation of the organic portion of the steam distillate (after the benzene and cyclooctatetraene present had been removed as low-boiling fractions). The substituted cyclooctatetraenes were purified by fractional distillation and through silver nitrate complexes.

Methylcyclooctatetraene (III).—Propyne⁸ (30 g.) was dissolved in 250 g. of tetrahydrofuran (which had been cooled with Dry Ice and trichloroethylene) and placed in the 1-l. autoclave, which also was cooled with Dry Ice. The copolymerization procedure described above was followed, with displacement of the air in the system before the mixture warmed to 0° to avoid loss of propyne. All of the product was isolated by fractionation of the organic portion of the steam distillate through a 45 × 1.5-cm. glass helix-packed column, which yielded benzene, about 40 g. of cyclooctatetraene and 14.1 g. (16%) of methylcyclooctatetraene, a yellow liquid, b. p. 86–88° (73 mm.), n_D^{25} 1.5248–1.5260. A pure sample of III was obtained by conversion to the crystalline silver nitrate complex (described below), regeneration by shaking with a 100% excess of concentrated ammonium hydroxide, extraction with pentane and redistillation; b. p. 84.5° (67 mm.), n_D^{25} 1.5249, d_4^{25} 0.8978.

Anal. Calcd. for C_9H_{10} : C, 91.47; H, 8.53. Found: C, 91.17; H, 8.35.

A small amount of toluene was isolated from a fraction of the distillate boiling higher than benzene and lower than cyclooctatetraene. The fraction was dissolved in pentane, washed with 50% aqueous silver nitrate to remove cyclooctatetraene, and redistilled to separate the toluene, b. p. 108–109°, n_D^{25} 1.4929, identified by its infrared spectrum.

Methylcyclooctatetraene-silver nitrate complex was prepared by adding 30.5 g. of finely powdered silver nitrate to a solution of 14.1 g. of III in 200 ml. of boiling absolute ethanol. The mixture was stirred and heated until all the silver nitrate dissolved, cooled, and filtered to separate the complex, which was washed on the funnel with dry ether. The yield was 40.0 g. (90%), m. p. 120–123°. Recrystallization from absolute ethanol followed by washing with ether and brief drying in a vacuum desiccator yielded the methylcyclooctatetraene-silver nitrate complex as compact light-yellow prisms with a constant melting point of 123–124.5° (opaque melt).

Anal. Calcd. for $2\text{C}_9\text{H}_{10} \cdot 3\text{AgNO}_3$: C, 28.98; H, 2.70; Ag, 43.38. Found: C, 29.22; H, 2.74; Ag, 43.25.

(7) Melting points are corrected and boiling points are uncorrected. The melting points of silver nitrate complexes were determined by introducing samples into a bath 10° below the melting point and raising the temperature 2° per minute. We are indebted to Mr. S. M. Nagy and his associates for analyses, and for the infrared spectra, which were determined with a Baird Double Beam Infrared Recording Spectrometer, Model B, fitted with a sodium chloride prism.

(8) Obtained from the Farchan Research Laboratories, Cleveland, Ohio.

Methylcyclooctatetraene-maleic anhydride adduct was prepared by heating a solution of 0.82 g. of III and 0.68 g. of maleic anhydride in 10 ml. of toluene under reflux for 18 hours. The solution was concentrated to 5 ml., and the white needles which separated on cooling (0.45 g., 30%, m. p. 139.5–142°) were purified by recrystallization from a mixture of benzene and petroleum ether and sublimation at 0.3 mm. and 135°; m. p. 141.5–142.5°.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.21; H, 5.60. Found: C, 71.97; H, 5.85.

Hydrogenation of a solution of 1.55 g. of III in 25 ml. of glacial acetic acid in the presence of 0.19 g. of pre-reduced platinum oxide was complete in 140 minutes and 97% of four molar equivalents of hydrogen was absorbed. The catalyst was separated, the filtrate was made basic with 30% sodium hydroxide with cooling, and the product was extracted with pentane. The extracts were washed with water, dried over magnesium sulfate, concentrated, and the residue was distilled through a semi-micro column,⁹ yielding 0.88 g. of methylcyclooctane, b. p. 97° (92 mm.), n_D^{25} 1.4529, d_4^{25} 0.8223, with an infrared spectrum identical with the authentic sample described below.

Anal. Calcd. for C_9H_{18} : C, 85.63; H, 14.37. Found: C, 85.94; H, 14.45.

Methylcyclooctane (IV).—Reaction of 1.56 g. of cyclooctanone with the methylmagnesium iodide prepared from 3.9 g. of methyl iodide and 0.61 g. of magnesium in ether, followed by dehydration of the 1-methylcyclooctanol with iodine,¹⁰ yielded 1-methylcyclooctene,¹¹ b. p. 87–90° (84 mm.), n_D^{25} 1.4682.

Anal. Calcd. for C_9H_{16} : C, 87.02; H, 12.98. Found: C, 87.05; H, 12.84.

Hydrogenation of a solution of 0.38 g. of 1-methylcyclooctene in 15 ml. of glacial acetic acid in the presence of 0.1 g. of pre-reduced platinum oxide was complete in 40 minutes and 97% of one molar equivalent of hydrogen was absorbed. Methylcyclooctane was isolated in the manner described above in a yield of 0.21 g., b. p. 94–95° (90 mm.), n_D^{25} 1.4519.¹²

Anal. Calcd. for C_9H_{18} : C, 85.63; H, 14.37. Found: C, 85.50; H, 14.13.

Mixture of Dimethylcyclooctatetraenes.—Higher boiling fractions obtained from several methylcyclooctatetraene preparations were combined and re-fractionated through a semi-micro column, and yielded 1.38 g. of a yellow mixture of dimethylcyclooctatetraenes, b. p. 86–89° (39 mm.), n_D^{25} 1.5280–1.5298, which in carbon and hydrogen analysis corresponded to the formula $C_{10}H_{12}$. A pentane solution of 1.05 g. of the mixture of isomers was extracted into 20 ml. of 50% aqueous silver nitrate (to separate any *cis*-1-phenyl-1,3-butadiene that might have been present¹⁰), and the hydrocarbons were regenerated from the extract by shaking it with 15 ml. of pentane, 10 g. of ice and 25 ml. of concentrated ammonium hydroxide. The pentane layer and a pentane extract of the aqueous layer were washed with water, dried over magnesium sulfate, concentrated, and the residue was distilled through a semi-micro column. The distillate had n_D^{25} 1.5205–1.5219. The ultraviolet absorption spectrum (Fig. 1) of a sample with n_D^{25} 1.5210 (compare n_D^{25} 1.5664 of vinylcyclooctatetraene,¹⁰ which has a similar boiling point) was practically identical with the spectrum of 1,2-dimethylcyclooctatetraene. Hydrogenation of a solution of 0.046 g. of a sample with n_D^{25} 1.5205 in 10 ml. of acetic acid in the presence of 0.1 g. of pre-reduced platinum oxide was complete in 30 minutes and the hydrogen absorption was 100% of four molar equivalents, based on the formula $C_{10}H_{12}$.

***n*-Propylcyclooctatetraene (V).**—1-Pentyne⁸ (27 g.) was employed in the copolymerization with acetylene according to the general procedure described above. The organic

(9) C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

(10) By a procedure similar to the one used for preparation of ethylcyclooctene by A. C. Cope and S. W. Fenton, *THIS JOURNAL*, **73**, 1195 (1951).

(11) M. Godchot and G. Cauquil, *Compt. rend.*, **185**, 1202 (1927).

(12) M. Godchot and G. Cauquil, *ibid.*, **191**, 1326 (1930), report n_D^{15} 1.4587, d_4^{15} 0.8405 for methylcyclooctane and n_D^{15} 1.4720 for methylcyclooctene. Analyses for the compounds were not reported and accordingly are included here.

layer in the steam distillate was dried over magnesium sulfate and fractionated through a 15 × 1.5-cm. glass helix-packed column, separating benzene and 53 g. of cyclooctatetraene from the crude product. A small amount of *n*-propylbenzene was isolated from the fraction intermediate in boiling point between cyclooctatetraene and *n*-propylcyclooctatetraene by the procedure used to isolate toluene from the methylcyclooctatetraene preparation. It was identified by boiling point (157°), refractive index (n_D^{25} 1.4903), and identity of the infrared spectrum with the spectrum of an authentic sample.

The high-boiling fraction from the steam distillate and the crude product obtained from the benzene extract of the residue from the steam distillate were combined and distilled, and yielded 23.2 g. of crude V, b. p. 83–94° (16 mm.). A solution of this crude product in 350 ml. of absolute ethanol was boiled with 54 g. of finely powdered silver nitrate until a homogeneous solution was obtained. The silver nitrate complex that separated on cooling was collected on a filter and decomposed by shaking with 50 ml. of pentane, 50 g. of ice, and 60 ml. of concentrated ammonium hydroxide. The aqueous layer was extracted with 25 ml. of pentane, and the combined pentane solutions were washed with water, dried over magnesium sulfate, concentrated and the residue was distilled. The yield of *n*-propylcyclooctatetraene was 14.4 g. (25%), b. p. 86–90° (18–20 mm.), n_D^{25} 1.5136–1.5142. A sample obtained from a similar preparation was analyzed; b. p. 73° (9 mm.), n_D^{25} 1.5131, d_4^{25} 0.8870.

Anal. Calcd. for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.47; H, 9.55.

***n*-Propylcyclooctatetraene-silver nitrate complex** was prepared by boiling a solution of 0.27 g. of V in 4 ml. of absolute ethanol with 0.47 g. of finely powdered silver nitrate. The crystalline complex that separated on cooling amounted to 0.56 g. (76%) and melted at 140.5° (dec.). Two recrystallizations from absolute ethanol yielded compact faintly yellow crystals with a constant melting point of 141° (dec.).

Anal. Calcd. for $C_{11}H_{14} \cdot 2AgNO_3$: C, 27.18; H, 2.90; Ag, 44.40. Found: C, 27.26; H, 2.99; Ag, 44.41.

Hydrogenation of a solution of 0.89 g. of V in 20 ml. of glacial acetic acid in the presence of 0.28 g. of pre-reduced platinum oxide was complete in 1 hour and 100% of four molar equivalents of hydrogen was absorbed. *n*-Propylcyclooctane (VI) was isolated in the manner described above for methylcyclooctane; 0.60 g., b. p. 86–87.5° (12 mm.), n_D^{25} 1.4571, d_4^{25} 0.8326.

Anal. Calcd. for $C_{11}H_{22}$: C, 85.62; H, 14.38. Found: C, 85.50; H, 14.14.

1,2-Dimethylcyclooctatetraene (VII).—2-Butyne⁸ (25.5 g.) was copolymerized with acetylene by the general procedure described. All of the product was isolated from the organic layer of the steam distillate, which was dried over magnesium sulfate and fractionated through a 15 × 1.5-cm. glass helix-packed column. Benzene and 52 g. of cyclooctatetraene were separated as low-boiling fractions, followed by 11.7 g. (19%) of 1,2-dimethylcyclooctatetraene, b. p. 102.5–106.5° (92 mm.), n_D^{25} 1.5238–1.5259. A sample of VII regenerated from its crystalline silver nitrate complex (described below) had b. p. 107° (96 mm.), n_D^{25} 1.5219, d_4^{25} 0.8950.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 91.01; H, 9.21.

A portion of the cyclooctatetraene fraction obtained in the preparation of VII was dissolved in pentane and extracted with 20% silver nitrate until the yellow color was removed. Distillation of the residue obtained by concentrating the pentane solution yielded a small amount of *o*-xylene contaminated with about 10% of styrene (identified by the infrared spectrum).

1,2-Dimethylcyclooctatetraene-silver nitrate complex was prepared by heating a solution of 0.20 g. of VII in 4 ml. of absolute ethanol with 0.51 g. of powdered silver nitrate. On cooling the solution 0.49 g. of the silver nitrate complex separated, m. p. 140–143.5°, which after recrystallization from absolute ethanol melted at 142.5–144.5° (opaque melt).

Anal. Calcd. for $C_{10}H_{12} \cdot 2AgNO_3$: C, 25.45; H, 2.56; Ag, 45.71. Found: C, 24.89; H, 2.86; Ag, 45.53.

1,2-Dimethylcyclooctatetraene-maleic anhydride adduct was prepared by heating a mixture of 0.44 g. of VII and

0.32 g. of maleic anhydride at 165° for 1 hour. The crude solid product was recrystallized from a mixture of benzene and cyclohexane, and yielded 0.52 g. (68%) of the adduct as long white needles melting at 178–181°. Sublimation at 0.3 mm. and 170–175° and three crystallizations from a mixture of benzene and cyclohexane furnished an analytical sample with a constant melting point of 184.5–185.5°.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 72.83; H, 6.38.

1,2-Dimethylcyclooctene (VIII).—A solution of 1.03 g. of 1,2-dimethylcyclooctatetraene in 15 ml. of dry methanol was hydrogenated in the presence of 0.5 g. of 1% palladium-on-calcium carbonate.¹³ The reduction stopped after 95 minutes, at which time 102% of three molar equivalents of hydrogen had been absorbed. The mixture was filtered, the filtrate was diluted with 25 ml. of water, and extracted twice with pentane. The extracts were washed with water, dried over magnesium sulfate, and distilled through a semi-micro column, yielding 0.71 g. (66%) of VIII, b. p. 101–102.5° (65 mm.), n_D^{25} 1.4709. The infrared spectrum of VIII (Fig. 3, curve 4) showed no definite evidence of absorption due to olefinic C–H in the 3 μ region, although a very faint shoulder on the short wave length side of the aliphatic C–H band might be an indication of the presence of olefinic C–H in small amount.¹⁴ This evidence and the ozonization described below provides the basis for assignment of structure VIII to the reduction product.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.75; H, 12.97.

1,2-Dimethylcyclooctane.—A solution of 0.51 g. of 1,2-dimethylcyclooctene in 15 ml. of acetic acid was hydrogenated in the presence of 0.15 g. of pre-reduced platinum oxide. The hydrogenation was complete in 75 minutes, and the uptake of hydrogen was 95% of one molar equivalent. The reduction product was isolated in the same manner as IV and amounted to 0.26 g. of 1,2-dimethylcyclooctane, b. p. 99–105° (70 mm.), n_D^{25} 1.4544–1.4559. A fraction with n_D^{25} 1.4558 was analyzed.

Anal. Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.68; H, 14.23.

Ozonization of 1,2-Dimethylcyclooctene.—A solution of 2.12 g. of 1,2-dimethylcyclooctene in 25 ml. of ethyl acetate was ozonized at –75° for 80 minutes with a stream of oxygen delivering 10 mg. of ozone per minute. The ozonide was decomposed by shaking the mixture with hydrogen in the presence of 0.5 g. of 10% palladium-on-Norit with cooling by Dry Ice for two hours, and for three hours longer after the Dry Ice was removed. After separating the catalyst and drying the filtrate over magnesium sulfate, distillation yielded 1.02 g. (39%) of decane-2,9-dione as a low-melting solid, b. p. 98–104° (1.7 mm.). Three crystallizations from 2,3-dimethylbutane yielded the diketone as large colorless plates with a constant melting point (and mixed melting point with a known sample described below) of 56–57°.¹⁵

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.51; H, 10.78.

Oxidation of a sample of the diketone with sodium hypobromite^{15a} yielded suberic acid, identified by its melting point and mixed melting point. Another sample was converted to the dioxime, which after recrystallization from ethanol and water and from benzene had a melting point (and mixed melting point with a known sample) of 131.5–132.5° (ref. 15a reports m. p. 132°).

An authentic sample of decane-2,9-dione was prepared from 5.3 g. of suberyl chloride^{15b} and dimethylcadmium under conditions used for similar preparations by Cason.¹⁶ The yield was 3.57 g. (84%), b. p. 89–93° (0.37 mm.). Purification of the solid distillate by two crystallizations

(13) M. Busch and H. Stove, *Ber.*, **49**, 1063 (1916).

(14) We are indebted to Dr. R. C. Lord for discussions of the infrared spectra.

(15) (a) I. M. Heilbron, E. R. H. Jones and R. A. Raphael, *J. Chem. Soc.*, 268 (1943), report m.p. 82°; (b) E. E. Blaise and A. Koehler, *Bull. soc. chim. France*, [4] **5**, 690 (1909), report m.p. 64°.

(16) J. Cason, *Chem. Revs.*, **40**, 23 (1947); *THIS JOURNAL*, **68**, 2078 (1946).

from 2,3-dimethylbutane and by sublimation at 0.3 mm. and 30–50° yielded a sample with a constant melting point of 56–57°. The dioxime prepared from this authentic sample melted at 131.5–132.5°.

Phenylcyclooctatetraene (I).—Phenylacetylene⁸ (20 g.) was copolymerized with acetylene by the general procedure described above, except that 5 g. of nickel cyanide¹⁷ was used in place of nickel acetylacetonate as the catalyst. The crude product isolated from the steam distillate and from the benzene extract of the residue from the steam distillation was converted to the crystalline silver nitrate complex by the procedure previously described, and subsequently regenerated from the adduct by treatment with ammonium hydroxide. Distillation through a semi-micro column yielded 6.1 g. (17%) of I, b. p. 101–103° (0.4–0.55 mm.), n_D^{25} 1.6181. The silver nitrate complex of I prepared from phenylacetylene melted at 143.5° (dec.) (ref. 6a reports m. p. 144.5° dec.), and the maleic anhydride adduct had a melting point and mixed melting point with an authentic sample^{6a} of 172–174°.

***n*-Butylcyclooctatetraene (II).**—1-Hexyne⁸ (20 g.) was copolymerized with acetylene by the general procedure described above. The organic layer of the steam distillate was dried over magnesium sulfate and distilled through an 18 × 1.8-cm. glass helix-packed column to separate benzene and 54 g. of cyclooctatetraene from crude II, which after distillation amounted to 12.9 g. An additional 6.2 g. was isolated from the benzene extract of the residue from the steam distillation. These crude fractions of II were combined, dissolved in pentane, washed with 85% phosphoric acid to remove azulene, and then extracted with two 20-ml. portions and twelve 10-ml. portions of 50% (by weight) aqueous silver nitrate to separate II from *cis*-1-phenyl-1,3-butadiene.¹⁰ *n*-Butylcyclooctatetraene was regenerated from the silver nitrate extracts by treatment with an excess of ammonium hydroxide, with cooling, and fractionated through a 15 × 1.5-cm. column packed with glass helices. The yield of II was 6.17 g. (16%), b. p. 87° (10 mm.), n_D^{25} 1.5092. The infrared spectrum was virtually identical with the spectrum of II prepared from cyclooctatetraene and *n*-butyllithium,^{6b} and contained no bands that would indicate contamination of the product with vinylcyclooctatetraene.

Hydrogenation of a solution of 1.47 g. of II in 25 ml. of acetic acid in the presence of 0.19 g. of pre-reduced platinum oxide was complete in 3 hours, and resulted in the absorption of 102% of four molar equivalents of hydrogen. The reduction product was 0.93 g. of *n*-butylcyclooctane, b. p. 95.5–96.5° (9 mm.), n_D^{25} 1.4591, identified by its infrared spectrum.^{6b}

Ethylcyclooctatetraene Derivatives.—The following crystalline derivatives were prepared to characterize ethylcyclooctatetraene (obtained from cyclooctatetraene and ethyllithium^{6b}).

Ethylcyclooctatetraene-silver nitrate complex was prepared by dissolving 0.433 g. of powdered silver nitrate in a boiling solution of 0.168 g. of ethylcyclooctatetraene in 3 ml. of absolute ethanol. The grayish-white crystals which separated (0.44 g., m. p. 116–118°) were recrystallized twice from absolute ethanol, washed with ether and dried briefly in a vacuum desiccator; m. p. 124–125.5° (opaque melt).

Anal. Calcd. for $C_{10}H_{12} \cdot 2AgNO_3$: C, 25.45; H, 2.56; Ag, 45.71. Found: C, 25.16; H, 2.86; Ag, 46.10.

Ethylcyclooctatetraene-maleic anhydride adduct was prepared by heating a mixture of 0.67 g. of ethylcyclooctatetraene and 0.47 g. of maleic anhydride at 165–170° for 1 hour. Recrystallization from a mixture of benzene and cyclohexane yielded 0.58 g. of white needles melting at 88–92.5°, and sublimation at 0.3 mm. and 85–88° followed by four crystallizations from benzene-cyclohexane and resublimation furnished an analytical sample with a constant melting point of 97–98.5°.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.01; H, 6.30.

CAMBRIDGE, MASSACHUSETTS

RECEIVED JULY 9, 1951

(17) "Inorganic Syntheses," McGraw-Hill Book Co., New York, N. Y., 1946, p. 288 (1951).