

0.79 g. (94%) of the amine oxide picrate, m.p. 150–151°. An analytical sample that was recrystallized from ethanol had the same melting point.

Anal. Calcd. for $C_{15}H_{22}N_4O_8$: C, 46.63; H, 5.74; N, 14.50. Found: C, 46.34; H, 5.77; N, 14.46.

A sample of *N,N*-dimethylcycloheptylamine oxide prepared from 8.0 g. of the amine was decomposed in a nitrogen atmosphere at 13 mm., with a bath temperature of 125–135°. The cycloheptene was isolated in the same manner as *cis*-cycloöctene (described above) in a yield of 5.07 g. (92%), b.p. 72° (300 mm.), n_D^{25} 1.4569. *N,N*-Dimethylhydroxylamine hydrochloride was isolated from the aqueous layer as before in a yield of 4.2 g. (76%).

Decomposition of the quaternary base prepared from 15 g. of *N,N,N*-trimethylcycloheptylammonium iodide¹ under the conditions described above for the amine oxide decomposition and isolation of the product in the same manner, yielded 4.35 g. (87%) of cycloheptene, b.p. 72° (300 mm.), n_D^{25} 1.4570. Cycloheptene also was prepared in 85% yield from 10 g. of cycloheptanol and 5.5 g. of boric acid, heated in a bath at 175 to 275°²⁵; b.p. 72° (300 mm.), n_D^{25} 1.4570. The cycloheptene samples prepared by these three methods had essentially identical infrared spectra.

(25) W. Brandenberg and A. Galot, *THIS JOURNAL*, **72**, 3275 (1950).

***N,N*-Dimethylcyclohexylamine Oxide and Cyclohexene.**—*N,N*-Dimethylcyclohexylamine oxide was prepared by the method described for *N,N*-dimethylcycloöctylamine oxide. A sample prepared from 0.277 g. of the amine was treated with an aqueous solution of 0.5 g. of picric acid, and yielded 0.75 g. (93%) of the amine oxide picrate, m.p. 153–154°. An analytical sample that was recrystallized from ethanol had the same melting point.

Anal. Calcd. for $C_{14}H_{20}N_4O_8$: C, 45.16; H, 5.42; N, 15.05. Found: C, 45.35; H, 5.55; N, 14.88.

A sample of *N,N*-dimethylcyclohexylamine oxide that was prepared from 9.50 g. of the amine was decomposed by heating in a nitrogen atmosphere at 11 mm. with a bath temperature of 145–160°. The cyclohexene formed was condensed in a trap cooled with liquid nitrogen and purified in the manner described above for *cis*-cycloöctene. The yield of cyclohexene was 5.11 g. (83%), and the yield of *N,N*-dimethylhydroxylamine hydrochloride was 6.8 g. (93%). Decomposition of the quaternary base prepared from 8.0 g. of *N,N,N*-trimethylcyclohexylammonium iodide² by the procedure described above yielded 1.5 g. (62%) of cyclohexene and 0.56 g. (15%) of *N,N*-dimethylcyclohexylamine. The infrared spectra of the two samples of cyclohexene and a purified commercial sample were identical.

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

Cyclic Polyolefins. XXVIII. Functionally Substituted Cycloöctatetraenes from Acetylenic Alcohols¹

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Cycloöctatetraenylmethyl alcohol (I) and β -cycloöctatetraenylethyl alcohol (III) have been prepared by copolymerization of acetylene with propargyl alcohol and 3-butyne-1-ol, respectively. *N,N*-Dimethyl- β -cycloöctatetraenylethylamine (V) also has been prepared by copolymerization. The *p*-toluenesulfonate of the alcohol III has proved to be a useful intermediate for the synthesis (by displacement reactions) of other cycloöctatetraene derivatives, including the *N,N*-dimethylamino compound V, the cyanide VII and the bromide X. Reduction of the cyanide VII with lithium aluminum hydride yielded the primary amine VIII without reduction of nuclear double bonds, and basic hydrolysis of the cyanide yielded β -cycloöctatetraenylpropionic acid (IX). The acid IX formed a crystalline salt with quinine, but could not be resolved through the salt under conditions that were examined. Absorption bands present in the infrared spectra of a number of cycloöctatetraene derivatives have been noted that appear to be characteristic of the nucleus and are useful for the identification of such compounds.

This paper reports an extension of the preparation of substituted cycloöctatetraenes by copolymerization of substituted acetylenes with acetylene² to the synthesis of cycloöctatetraene derivatives containing an alcoholic hydroxyl or dimethylamino group attached to an alkyl side chain. These compounds were prepared by copolymerization of acetylenic alcohols and an acetylenic amine with acetylene. Other cycloöctatetraene derivatives were prepared by utilizing β -cycloöctatetraenylethyl alcohol as an intermediate.

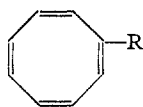
Copolymerizations of the functionally substituted acetylenes with acetylene were conducted in dry tetrahydrofuran in the presence of nickel acetylacetonate catalyst and calcium carbide as a drying agent in a stirred autoclave at 85–95° with acetylene pressures of 300–150 p.s.i. The volatile products formed from such copolymerizations with propargyl alcohol and 3-butyne-1-ol were separated by steam distillation, and the crude alcohols (cycloöctatetraenylmethyl alcohol, I, and β -cycloöctatetraenylethyl alcohol, III) were isolated by frac-

tionation of the organic portions of the distillates. The alcohols could not be separated completely from hydrocarbon impurities by distillation, but it was possible to purify them by chromatography on silica gel, from which they were eluted with pentane containing 1 to 10% of ether, after elution of the hydrocarbons with pentane. The pure alcohols I and III were obtained in 17 and 24% yields, respectively. Both were yellow liquids which formed crystalline 3,5-dinitrobenzoates. Quantitative hydrogenations of the two alcohols in the presence of platinum resulted in the absorption of 98.5% of four molar equivalents of hydrogen and formed the colorless, saturated alcohols, cycloöctylmethyl alcohol (II), and β -cycloöctylethyl alcohol (IV). Both II and IV were characterized by preparation of crystalline 3,5-dinitrobenzoates. The structures of these compounds were proved by independent synthesis of authentic samples of the saturated alcohols II and IV by treating cycloöctylmagnesium bromide with formaldehyde and ethylene oxide, respectively.

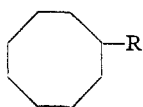
N,N-Dimethyl- β -cycloöctatetraenylethylamine (V) also was prepared by copolymerization, from acetylene and *N,N*-dimethyl-3-butyneamine.

(1) Supported in part by the Office of Naval Research under Contract N5ori-07822, Project Designation NR356-096.

(2) A. C. Cope and H. C. Campbell, *THIS JOURNAL*, **73**, 3536 (1951); **74**, 179 (1952).



- I, R = CH₂OH
 III, R = CH₂CH₂OH
 V, R = CH₂CH₂N(CH₃)₂
 VI, R = CH₂CH₂OSO₂C₆H₄CH₃(-*p*)
 VII, R = CH₂CH₂CN
 VIII, R = CH₂CH₂CH₂NH₂
 IX, R = CH₂CH₂COOH
 X, R = CH₂CH₂Br
 XI, R = CH₂CH₂OCOCH₃



- II, R = CH₂OH
 IV, R = CH₂CH₂OH

β -Cyclooctatetraenylethyl alcohol reacted with *p*-toluenesulfonyl chloride in pyridine to form the *p*-toluenesulfonate VI in a yield of 80–90% (crude). This ester failed to crystallize from a number of solvents, and decomposed on attempted distillation at low pressures. However, it could be used as an intermediate in displacement reactions without purification, in the same way that *p*-toluenesulfonates of acetylenic alcohols have been used recently.³ Reaction of the *p*-toluenesulfonate VI with dimethylamine yielded N,N-dimethyl- β -cyclooctatetraenylethylamine (V) (45%). This method of preparation of V is preferable to the copolymerization of N,N-dimethyl-3-butynylamine with acetylene. Reaction of the *p*-toluenesulfonate VI with calcium bromide in Methyl Cellosolve formed β -cyclooctatetraenylethyl bromide (X), which also was prepared from the alcohol III and phosphorus tribromide in the presence of pyridine. The bromide X obtained by both routes was slightly impure because of partial dehydrobromination that occurred during distillation, but it was used in an alternate synthesis of the amine V (reaction with dimethylamine).

The reaction of the *p*-toluenesulfonate VI with potassium cyanide in aqueous ethanol yielded β -cyclooctatetraenylethyl cyanide (VII) (78%). Reduction of this yellow liquid nitrile with lithium aluminum hydride in ether yielded γ -cyclooctatetraenylpropylamine (VIII) (56%), a yellow liquid that was characterized as the picrate and the hydrochloride. Saponification of the nitrile VII yielded the yellow, crystalline β -cyclooctatetraenylpropionic acid (IX) (77%). The acid IX formed a crystalline salt with quinine, but the acid regenerated from the salt after recrystallization to constant melting point and rotation was optically inactive. Other attempts to resolve monosubstituted cyclooctatetraenes also have been unsuccessful.⁴

β -Cyclooctatetraenylethyl acetate (XI), a fragrant, yellow liquid, was prepared in 91% yield from the alcohol III and acetic anhydride.

Spectra and Structure.⁵—The infrared spectra of the cyclooctatetraene derivatives I, III, V, VII, VIII, IX and XI are reproduced in Figs. 2, 3 and 4. Examination of these spectra and the spectra of other monosubstituted cyclooctatetraenes reported previously (ref. 2 and preceding papers in this series), and in the following paper (no. XXIX), shows that characteristic absorption bands

can be assigned to such compounds. The infrared spectrum of cyclooctatetraene itself has been discussed in detail by Lippincott, Lord and McDonald.⁶ Comparison of the principal absorption bands of cyclooctatetraene and monosubstituted cyclooctatetraenes shows certain differences. The principal absorption bands (and their probable origins) that are present in the spectra of all monosubstituted cyclooctatetraenes examined to date are the following: 3.33 μ (strong) (C–H stretching); 6.1–6.15 μ (medium) (double bond in a cyclooctatetraene ring); 8.20–8.33 μ (doublet, weak) (C–H bending); 11.3–11.6 μ (medium) (ring expansion); 12.3–12.5 μ (strong) and 12.8–13.0 μ (medium) (doublet associated with ring distortion vibrations); 14.25–14.55 μ (strong) (C–H bending); 15.0–15.25 μ (medium) (C–H bending).

The ultraviolet absorption spectra of cyclooctatetraene and its derivatives that do not contain a chromophore in conjugation with the nuclear double bonds (such as the alcohols I and III, Fig. 1) also are characteristic. They show weak absorption ($\log \epsilon$ less than 2.8) extending from the visible to about 230 m μ , where strong absorption begins. Other highly unsaturated compounds such as conjugated cyclic and acyclic trienes and acyclic tetraenes have distinct maxima in the ultraviolet at longer wave lengths. On the other hand, the weak visible absorption of cyclooctatetraene derivatives gives rise to a characteristic yellow color. A combination of the infrared absorption bands noted above, characteristic ultraviolet spectrum and yellow color with chemical evidence now can be used with considerable certainty to establish the structure of a new cyclooctatetraene derivative. The most pertinent chemical evidence is quantitative catalytic reduction with the absorption of four molar equivalents of hydrogen by the four nuclear double bonds. Other chemical characteristics that have been explored less thoroughly but have been useful in characterizing certain cyclooctatetraene derivatives have been partial reduction with absorption of three molar equivalents of hydrogen in the presence of palladium on calcium carbonate forming cyclooctene derivatives; formation of silver nitrate complexes, or solubility in aqueous silver nitrate; formation of maleic anhydride adducts with disappearance of two of the nuclear double bonds (due to bridging as well as addition).

Experimental⁷

Copolymerization and Purification Procedures.—The copolymerization procedure described previously² was followed, after which the mixture was steam distilled until 4 l. of distillate collected to separate volatile products. The organic layer was separated from the distillate, and the aqueous layer was extracted several times with benzene. The combined organic layer and extracts were distilled through a packed column under reduced pressure to separate tetrahydrofuran, benzene and cyclooctatetraene, and the residue

(6) E. R. Lippincott, R. C. Lord and R. S. McDonald, *THIS JOURNAL*, **73**, 3370 (1951).

(7) Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. 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.

(3) G. Eglington and M. C. Whiting, *J. Chem. Soc.*, 3650 (1950).

(4) A. C. Cope and M. R. Kinter, *THIS JOURNAL*, **73**, 3424 (1951);

A. C. Cope, M. Burg and S. W. Feuton, *ibid.*, **74**, 173 (1952).

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

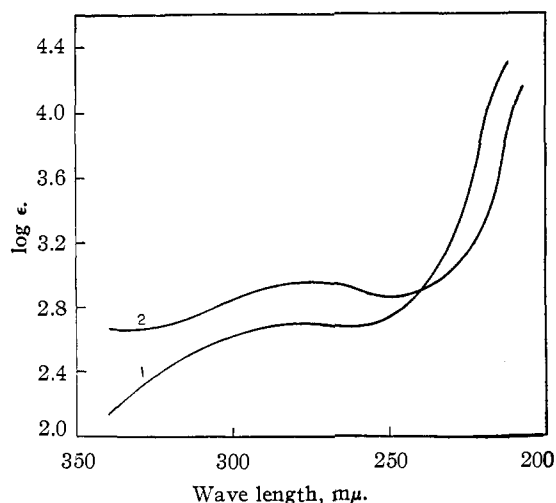


Fig. 1.—Ultraviolet absorption spectra: curve 1, cyclooctatetraenylmethyl alcohol (I); curve 2, β -cyclooctatetraenylethyl alcohol (III), both in cyclohexane, determined with a Cary Ultraviolet Recording Spectrophotometer, Model 11 MS.

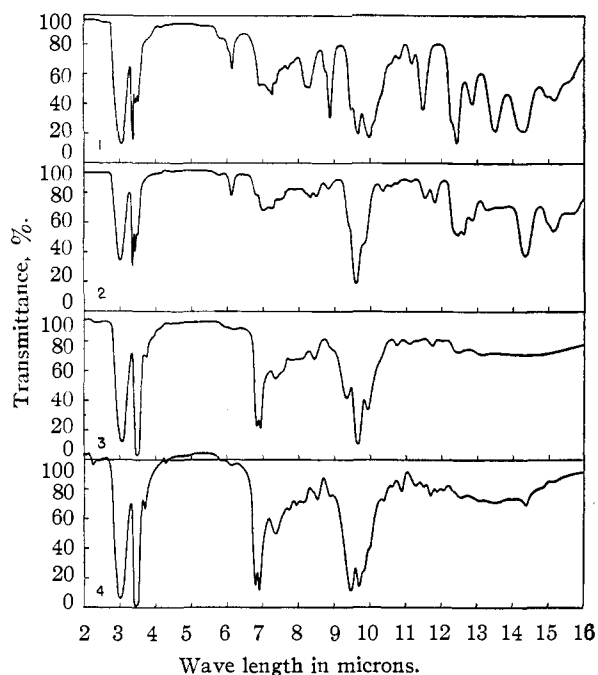


Fig. 2.—Infrared absorption spectra: curve 1, cyclooctatetraenylmethyl alcohol (I); curve 2, β -cyclooctatetraenylethyl alcohol (III); curve 3, cyclooctylmethyl alcohol (II); curve 4, β -cyclooctylethyl alcohol (IV), all as pure liquids in a 0.025-mm. cell.

was fractionated through a semimicro column⁸ at about 1 mm. The crude copolymerization products, containing hydrocarbons with similar boiling points as impurities, were dissolved in pentane and passed through a 100 \times 2.1-cm. column of 28 to 200 mesh silica gel (De-ison Chemical Corporation). The functionally substituted cyclooctatetraenes were adsorbed, while the hydrocarbons passed through with the solvent and were removed by washing with pentane. The substituted cyclooctatetraenes were eluted with 1-10% solutions of ether in pentane, and were isolated by concentration and fractional distillation.

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

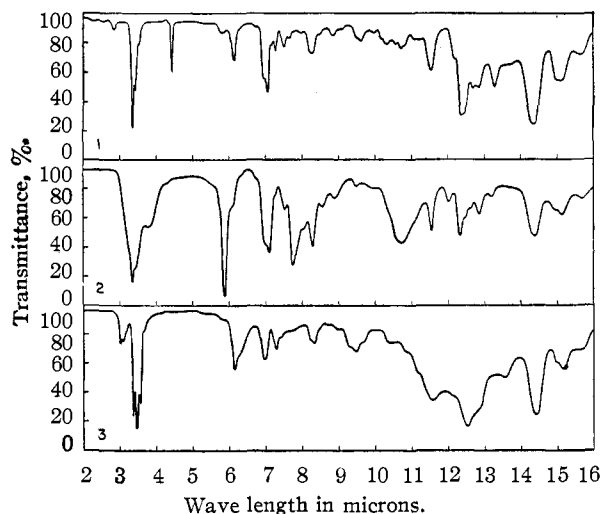


Fig. 3.—Infrared absorption spectra: curve 1, β -cyclooctatetraenylethyl cyanide (VII); curve 2, β -cyclooctatetraenylpropionic acid (IX); curve 3, γ -cyclooctatetraenylpropylamine (VIII). Curves 1 and 3 were determined for the pure liquids in a 0.025-mm. cell, and curve 2 for solutions (100 mg./ml.) in carbon tetrachloride in the region 2.0-7.9 μ and in carbon disulfide in the region 7.9-16.0 μ , in a 0.10-mm. cell.

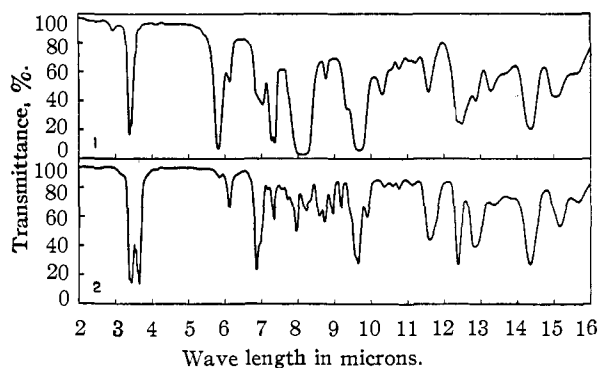


Fig. 4.—Infrared absorption spectra: curve 1, β -cyclooctatetraenylethyl acetate (XI); curve 2, *N,N*-dimethyl- β -cyclooctatetraenylethylamine (V), both as pure liquids in a 0.025-mm. cell.

Cyclooctatetraenylmethyl Alcohol (I).—Copolymerization of acetylene with 20 g. of propargyl alcohol (General Aniline and Film Corp., redistilled, b.p. 45-48° at 32 mm., n_D^{25} 1.4290) by the general procedure previously described² resulted in absorption of 950 p.s.i. of acetylene. Distillation yielded 9.9 g. (21%) of crude I, b.p. 66-72° (0.5 mm.), n_D^{25} 1.5602-1.5620. The alcohol was chromatographed by the procedure described above, and eluted with 3 l. of ether-pentane (1:9). Concentration of the effluent and distillation of the residue through a semimicro column⁸ yielded 8.1 g. (17%) of pure I as a yellow liquid, b.p. 65-66° (0.12 mm.), n_D^{25} 1.5612, d_4^{25} 1.0473.

Anal. Calcd. for $C_8H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.63; H, 7.66.

Cyclooctatetraenylmethyl 3,5-dinitrobenzoate was prepared by heating 0.25 g. of I and 0.35 g. of 3,5-dinitrobenzoyl chloride on a steam-bath for 1 minute. The product was dissolved in 10 ml. of hexane and cooled, and the yellow crystalline ester that separated was recrystallized to constant melting point from hexane; yield 0.43 g. (73%), m.p. 69-69.8°.

Anal. Calcd. for $C_{16}H_{12}N_2O_6$: C, 58.54; H, 3.69; N, 8.54. Found: C, 58.32; H, 3.78; N, 8.73.

Cyclooctylmethyl alcohol (II) was obtained by hydrogenation of a solution of 0.11 g. of I in 10 ml. of 95% ethanol in

the presence of 0.05 g. of prerduced platinum oxide. Hydrogen absorption stopped after uptake of 98.5% of 4 molar equivalents in 3 hours. Separation of the catalyst and distillation yielded 0.11 g. of II, b.p. 66–68° (0.15 mm.), n_D^{25} 1.4810, d_4^{25} 0.9426.

Anal. Calcd. for $C_8H_{10}O$: C, 76.00; H, 12.75. Found: C, 76.28; H, 12.82.

Cyclooctylmethyl 3,5-dinitrobenzoate was prepared by heating 0.20 g. of II and 0.27 g. of 3,5-dinitrobenzoyl chloride on a steam-bath for 1 hour, and purified by recrystallization from hexane; yield 0.33 g. (69%), m.p. 68.6–69.7°.

Anal. Calcd. for $C_{16}H_{20}N_2O_6$: C, 57.13; H, 5.99; N, 8.33. Found: C, 57.21; H, 6.06; N, 8.37.

An authentic sample of cyclooctylmethyl alcohol was prepared in poor (15%) yield from cyclooctylmagnesium bromide and formaldehyde. The authentic sample had the same physical constants (b.p. 67–68° at 0.20 mm., n_D^{25} 1.4810) as II obtained from I by hydrogenation, and formed an identical 3,5-dinitrobenzoate (m.p. and mixed m.p. 68.5–69.6°).

β -Cyclooctatetraenylethyl Alcohol (III).—Copolymerization of acetylene with 15 g. of 3-butyn-1-ol (Farchan Research Laboratories, redistilled) by the procedure previously described² resulted in absorption of 1200 p.s.i. of acetylene and an increase in weight of 178 g. in 11 hours at 80–95°. Distillation yielded 69 g. of cyclooctatetraene and 12 g. of crude III, b.p. 63–75° (0.55 mm.). The product was chromatographed on silica gel by the procedure described above, and eluted with 3 l. of pentane containing 2% ether. Concentration of the effluent and fractionation of the residue yielded 8.1 g. (24%) of III, b.p. 75–78° (0.22 mm.), n_D^{25} 1.5448–1.5480. A redistilled analytical sample had b.p. 77–78° (0.2 mm.), n_D^{25} 1.5480, d_4^{25} 1.0213.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.17. Found: C, 81.10; H, 8.39.

Purification of the alcohol III also was effected by dissolving it in concentrated phosphoric acid, extracting the solution several times with ether (extracts were discarded), and neutralizing with 10% sodium hydroxide, with cooling. Extraction with ether and distillation yielded pure III, but about half of the material was lost by polymerization during the acid treatment. Fairly pure samples of III also were obtained by extracting the crude alcohol with 20% (by weight) aqueous silver nitrate, and regenerating the alcohol from the aqueous solution containing III as a silver nitrate complex by treatment with an excess of concentrated ammonium hydroxide.

β -Cyclooctatetraenylethyl 3,5-dinitrobenzoate was obtained by adding 1.1 g. of 3,5-dinitrobenzoyl chloride to a solution of 0.75 g. of III in 2 ml. of hexane, and heating on a steam-bath for 2 minutes. On cooling the mixture overnight 0.91 g. (53%) of the ester separated as yellow crystals. Two recrystallizations from a mixture of ethanol and water gave an analytical sample with a constant melting point of 67–67.8°.

Anal. Calcd. for $C_{17}H_{14}N_2O_6$: C, 59.65; H, 4.12; N, 8.19. Found: C, 59.95; H, 4.27; N, 8.13.

β -Cyclooctylethyl alcohol (IV) was obtained by hydrogenating a solution of 0.11 g. of III in 5 ml. of 95% ethanol in the presence of 0.05 g. of prerduced platinum oxide catalyst. After 2.5 hours 98.5% of four molar equivalents of hydrogen had been absorbed, and the reduction stopped. Removal of the catalyst and distillation yielded 0.098 g. of IV as a colorless liquid, b.p. 78–79° (0.2 mm.), n_D^{25} 1.4825, d_4^{25} 0.9360.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 77.15; H, 13.06.

β -Cyclooctylethyl 3,5-dinitrobenzoate was prepared by heating 0.15 g. of IV and 0.20 g. of 3,5-dinitrobenzoyl chloride in 5 ml. of hexane on a steam-bath for 1 minute. Cooling in ice followed by two crystallizations from petroleum ether of the light yellow crystals that formed yielded 0.19 g. (54%) of the ester, m.p. 46.5–47.8°.

Anal. Calcd. for $C_{17}H_{22}N_2O_6$: C, 58.27; H, 6.33; N, 8.02. Found: C, 58.04; H, 6.43; N, 8.17.

An authentic sample of the alcohol IV was prepared in 26% yield by heating cyclooctylmagnesium bromide with an excess of ethylene oxide in a mixture of ether and benzene at 65° for 1 hour. The authentic sample had b.p. 77.5–78.5° (0.2 mm.), n_D^{25} 1.4821, and an infrared spectrum that was

identical within the limits of experimental error with IV prepared by reduction of III. The 3,5-dinitrobenzoate of the authentic sample of IV melted at 46.2–47.5° and was identical with the corresponding derivative of IV prepared from III (mixed m.p.).

4-Chloro-1-butyne.—A solution of 60 g. of thionyl chloride in 40 ml. of dry chloroform was added with stirring over a 2-hour period to a mixture of 28 g. of 3-butyn-1-ol, 15 g. of pyridine and 40 ml. of chloroform. The mixture was cooled in ice during the addition, and stirred at room temperature for 12 hours. The mixture was washed twice with water, once with 5% sodium bicarbonate solution, and dried over sodium sulfate. After removal of the chloroform under reduced pressure, distillation of the residue yielded 20.6 g. of crude 4-chloro-1-butyne, b.p. 75–85°. On redistillation 14.2 g. (40%) of the analytically pure chloride was obtained, with physical properties (b.p. 84–85°, n_D^{25} 1.4376) corresponding to those reported recently for 4-chloro-1-butyne prepared from 3-butyn-1-yl *p*-toluenesulfonate and lithium chloride (ref. 3, p. 3654).

N,N-Dimethyl-3-butyneamine.—A mixture of 25 g. of 4-chloro-1-butyne and 180 g. of 25% aqueous dimethylamine was stirred at room temperature for 3 days. The mixture was made strongly basic with 10% sodium hydroxide solution and extracted several times with ether. The extracts were dried over sodium sulfate, and the ether was removed through a packed column. Distillation of the residue yielded 18.8 g. of crude N,N-dimethyl-3-butyneamine, b.p. 89–106°, and redistillation gave 12.2 g. (45%) of the pure amine, b.p. 104–106°, n_D^{25} 1.4294, d_4^{25} 0.8111.

Anal. Calcd. for $C_6H_{11}N$: C, 74.16; H, 11.43; N, 14.42. Found: C, 73.88; H, 11.49; N, 14.31.

N,N-Dimethyl- β -cyclooctatetraenylethylamine (V) (a).—In the preferred preparation of V, a solution of 3.0 g. of β -cyclooctatetraenylethyl *p*-toluenesulfonate (VI, described below) in 15 ml. of benzene was saturated with gaseous dimethylamine. The mixture was allowed to stand overnight, and after washing with water was concentrated under reduced pressure. The residue was distilled at 55° (0.2 mm.), and a solution of the distillate in ether was extracted with excess 6 *N* hydrochloric acid. The acid solution was treated with excess sodium bicarbonate solution, and the amine V was extracted with ether. The extracts were dried over sodium sulfate, concentrated, and the residue was distilled through a semimicro column, yielding 0.94 g. (53%) of V, b.p. 59° (0.28 mm.), n_D^{25} 1.5198, d_4^{25} 0.9186.

Anal. Calcd. for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.47; H, 9.73; N, 7.86.

N,N-Dimethyl- β -cyclooctatetraenylethylamine picrate was prepared by adding an ethereal solution of picric acid to a solution of V in ether, and recrystallized from 95% ethanol to a constant melting point of 118.0–118.5°.

Anal. Calcd. for $C_{18}H_{20}N_4O_7$: C, 53.46; H, 4.98; N, 13.86. Found: C, 53.57; H, 4.99; N, 13.81.

N,N-Dimethyl- β -cyclooctatetraenylethylamine hydrochloride was prepared by passing dry hydrogen chloride through a solution of 0.63 g. of V in 10 ml. of dry ether. The crystalline hydrochloride was recrystallized twice to a constant m.p. of 179.6–180.6° from methanol-ether; yield 0.62 g. (82%).

Anal. Calcd. for $C_{12}H_{18}NCl$: C, 68.07; H, 8.57; N, 6.62. Found: C, 68.02; H, 8.72; N, 6.50.

(b).—Copolymerization of 10.7 g. of N,N-dimethyl-3-butyneamine with acetylene by the general procedure described previously² resulted in absorption of 800 p.s.i. of acetylene. The reaction mixture was centrifuged to remove solids and the clear liquid obtained was distilled under reduced pressure through a packed column to remove tetrahydrofuran and benzene. The residue was extracted with 3% hydrochloric acid; distillation of the neutral fraction yielded 30 g. of cyclooctatetraene. The acidic extracts were made basic with 10% sodium hydroxide and extracted with ether. After removal of the ether, distillation of the residue through a semimicro column yielded 1.5 g. (8%) of V with physical properties corresponding closely to the properties of V described under (a) above. The picrate of V prepared by copolymerization was analytically pure, and had m.p. and mixed m.p. with the picrate of V described under (a) of 117.5–118.5°.

β -Cyclooctatetraenylethyl *p*-Toluenesulfonate (VI).—A mixture of 14.5 g. of *p*-toluenesulfonyl chloride and 5.4 g. of

pyridine was added to 10.0 g. of the alcohol III, with cooling. Heat was evolved, and in a few minutes separation of crystalline pyridine hydrochloride began. After the mixture stood at room temperature for 12 hours, it was added to 150 ml. of 10% hydrochloric acid and extracted with ether several times. The extracts were dried over magnesium sulfate, concentrated, and the residue was evacuated at 0.2 mm. at room temperature for 15 minutes to complete removal of the solvent. The liquid residue of VI amounted to 20.2 g. (92%); it failed to crystallize, and was used as an intermediate without further purification.

β -Cyclooctatetraenylethyl Cyanide (VII).—A solution of 20.0 g. of the *p*-toluenesulfonate VI and 7.3 g. of potassium cyanide in 50 ml. of 90% ethanol was heated under reflux for 14 hours. After cooling, 100 ml. of water was added and the mixture was extracted with ether several times. The extracts were dried over magnesium sulfate, concentrated, and the residue was distilled through a semimicro column, yielding 8.3 g. (78%) of VII, b.p. 55–65° (0.25 mm.), n_D^{25} 1.5374–1.5385. A redistilled analytical sample had b.p. 62–63° (0.25 mm.), n_D^{25} 1.5378, d_4^{25} 0.9853.

Anal. Calcd. for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91. Found: C, 84.06; H, 7.11; N, 8.61.

γ -Cyclooctatetraenylpropylamine (VIII).—A solution of 2.0 g. of the nitrile VII in 15 ml. of dry ether was added slowly with stirring to 0.48 g. of lithium aluminum hydride in an atmosphere of nitrogen. The mixture was heated under reflux for 1 hour, cooled, and a small amount of water was added cautiously, followed by 35 ml. of 10% hydrochloric acid. The mixture was extracted with ether (extracts discarded), and then made basic with 10% sodium hydroxide. The amine VIII was extracted with ether, and the extracts were dried over magnesium sulfate and concentrated by distillation through a packed column. Two fractionations of the residue through a semimicro column yielded 1.15 g. (56%) of VIII, b.p. 68–68.5° (0.1 mm.), n_D^{25} 1.5411, d_4^{25} 0.9613.

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.93; H, 9.38. Found: C, 82.01; H, 9.51.

γ -Cyclooctatetraenylpropylamine picrate was obtained as yellow crystals by adding VIII to a saturated solution of picric acid in ethanol, and purified to a constant melting point of 166–167.5° by recrystallization from ethanol and water.

Anal. Calcd. for $C_{17}H_{18}N_4O_7$: C, 52.31; H, 4.65; N, 14.35. Found: C, 52.30; H, 4.93; N, 14.08.

γ -Cyclooctatetraenylpropylamine hydrochloride was prepared by passing hydrogen chloride through a solution of VIII in dry ether. The solid hydrochloride was recrystallized twice from methanol-ether to a constant melting point of 153.3–154.2°; yield 0.65 g. (84%).

Anal. Calcd. for $C_{11}H_{16}ClN$: C, 66.82; H, 8.16; N, 7.09. Found: C, 66.57; H, 8.15; N, 7.04.

β -Cyclooctatetraenylpropionic Acid (IX).—The nitrile VII (2.0 g.) was added to a solution of 2.0 g. of sodium hydroxide in 50 ml. of water, and the mixture was heated under reflux

for 4 hours, during which time it became homogeneous. After cooling, the solution was extracted with ether (extracts discarded), made strongly acidic with 10% hydrochloric acid, and extracted several times with ether. The liquid residue obtained on concentration of the extracts solidified as light yellow crystals (2.01 g., 90%). Three crystallizations from hexane yielded 1.7 g. (77%) of the pure acid IX, m.p. 59.2–60°.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87. Found: C, 74.98; H, 6.98.

The quinine salt of β -cyclooctatetraenylpropionic acid was prepared by adding a solution of 0.5 g. of the acid IX in 5 ml. of dry ether to a solution of 1.06 g. of quinine hydrate in 200 ml. of ether. The solution was concentrated to a volume of 50 ml. and cooled overnight at 5°. The yellow crystals that formed were recrystallized three times from ether without change in melting point or rotation; m.p. 119.6–120.6°, $[\alpha]_D^{25}$ 123.1° ($l = 2$, c 0.83 in 95% ethanol).

Anal. Calcd. for $C_{21}H_{26}N_4O_2$: C, 74.37; H, 7.25; N, 5.60. Found: C, 74.21; H, 7.25; N, 5.70.

Treatment of the quinine salt with 1% hydrochloric acid followed by extraction with ether yielded the pure acid IX, which was optically inactive.

β -Cyclooctatetraenylethyl Bromide (X).—The *p*-toluenesulfonate VI (14.4 g.) was allowed to react with 9.4 g. of anhydrous calcium bromide in 25 ml. of Methyl Cellosolve at 50° for 15 minutes. The mixture was cooled, added to 200 ml. of ether, and the calcium *p*-toluenesulfonate was separated by filtration (8.8 g., 96%). The filtrate was washed with water to remove Methyl Cellosolve, dried over magnesium sulfate, and distilled. The yield of the crude bromide X was 7.1 g. (72%), b.p. 61–67° (0.12 mm.), n_D^{25} 1.5580–1.5650. The product was chromatographed on silica gel to separate oxygen-containing impurities and refractionated several times, but pure X was not obtained, apparently because of some elimination of hydrogen bromide during the purification process. Fairly pure X obtained by this procedure had b.p. 65–67° (0.13 mm.), n_D^{25} 1.5686, d_4^{25} 1.2550.

Anal. Calcd. for $C_{10}H_{11}Br$: C, 56.89; H, 5.25. Found: C, 57.80; H, 5.47.

A similar slightly impure sample of X was obtained from reaction of the alcohol III with phosphorus tribromide in hexane, in the presence of pyridine. Reaction of the bromide X with dimethylamine yielded the tertiary amine V, which was obtained more easily from the *p*-toluenesulfonate VI.

β -Cyclooctatetraenylethyl Acetate (XI).—A mixture of 3.0 g. of the alcohol III and 4.1 g. of acetic anhydride was heated on a steam-bath for 20 minutes, cooled and added to 100 ml. of water. The product was extracted with several portions of benzene, which were dried over magnesium sulfate and concentrated. Distillation of the residue yielded 3.5 g. (91%) of the acetate XI as a fragrant, yellow liquid, b.p. 81–82° (0.15 mm.), n_D^{25} 1.5130, d_4^{25} 1.0260.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.56; H, 7.58.

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