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

Cyclic Polyolefins. XXIX. Cycloöctatetraene Derivatives from Copolymerization and Side Chain Modification[1]

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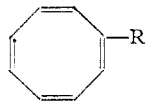
γ-Cycloöctatetraenyl-*n*-propyl alcohol (I), γ-cycloöctatetraenyl-*n*-propyl cyanide (V), cycloöctatetraenylmethylcarbinol (VIII), cycloöctatetraenyl methyl ketone (IX) and cycloöctatetraenyldimethylcarbinol (XI) have been prepared by copolymerization of acetylene with functionally substituted acetylenes. N,N-Dimethyl-γ-cycloöctatetraenyl-*n*-propylamine (IV) and γ-cycloöctatetraenyl-*n*-propyl cyanide (V) were prepared by displacement reactions of the *p*-toluenesulfonate III of the alcohol I, and δ-cycloöctatetraenyl-*n*-butylamine (VI) and γ-cycloöctatetraenyl-*n*-butyric acid (VII) by reduction and saponification, respectively, of the cyanide V. The structures of several of the new cycloöctatetraene derivatives were established by conversion to, or preparation from, known cycloöctatetraenes: The primary alcohol I was oxidized to β-cycloöctatetraenylpropionic acid (II); cycloöctatetraenylmethylcarbinol (VIII) was oxidized with sodium hypobromite to cycloöctatetraenecarboxylic acid; cycloöctatetraenyl methyl ketone (IX) was prepared by oxidation of the carbinol VIII; and cycloöctatetraenyldimethylcarbinol (XI) was prepared from methyl cycloöctatetraenecarboxylate and methylmagnesium iodide.

This paper reports the preparation of additional monosubstituted cycloöctatetraenes by two routes; copolymerization of acetylene with monosubstituted acetylenes, and chemical reactions of functional groups in the side chains of cycloöctatetraenes prepared by copolymerization. New cycloöctatetraenes prepared by copolymerization were the following: γ-cycloöctatetraenyl-*n*-propyl alcohol (I) (8%) from 4-pentyn-1-ol; γ-cycloöctatetraenyl-*n*-propyl cyanide (V) (11%) from 5-hexynenitrile; cycloöctatetraenylmethylcarbinol (VIII) (11%) from 3-butyn-2-ol; cycloöctatetraenyl methyl ketone (IX) (1.5%) from 3-butyn-2-one; cycloöctatetraenyldimethylcarbinol (XI) (13%) from 2-methyl-3-butyn-2-ol. These compounds were isolated and purified by a combination of steam distillation, fractionation and chromatography on silica gel described previously.[2] Physical evidence for their structures was provided by their infrared spectra (Figs. 1 and 2), which had the characteristics previously noted for monosubstituted cycloöctatetraenes.[2] Chemical evidence for the structure of γ-cycloöctatetraenyl-*n*-propyl alcohol (I) was obtained by oxidation with chromic acid to the known[2] crystalline β-cycloöctatetraenylpropionic acid (II) in 37% yield. Oxidation of cycloöctatetraenylmethylcarbinol (VIII) provided evidence for its structure and also for the structure of the ketone IX. Oxidation with chromic acid or Oppenauer oxidation with acetone and aluminum *t*-butoxide yielded cycloöctatetraenyl methyl ketone (IX) (also prepared by copolymerization), while oxidation with sodium hypobromite formed the known[3] crystalline cycloöctatetraenecarboxylic acid. The structure of cycloöctatetraenyldimethylcarbinol (XI) was verified by an independent synthesis from methyl cycloöctatetraenecarboxylate[3] and methylmagnesium iodide.



I, R = $(CH_2)_3OH$
II, R = $(CH_2)_2COOH$
III, R = $(CH_2)_3OSO_2C_6H_4CH_3(-p)$
IV, R = $(CH_2)_3N(CH_3)_2$
V, R = $(CH_2)_3CN$
VI, R = $(CH_2)_4NH_2$
VII, R = $(CH_2)_3COOH$
VIII, R = $CH(OH)CH_3$
IX, R = $COCH_3$
X, R = $C(=NOH)CH_3$
XI, R = $C(OH)(CH_3)_2$

γ-Cycloöctatetraenyl-*n*-propyl *p*-toluenesulfonate (III) was prepared from the alcohol I and *p*-toluenesulfonyl chloride in pyridine and used as an intermediate in the preparation of other cycloöctatetraenes in the manner previously reported for the next lower homolog.[2] Reaction of the *p*-toluenesulfonate III with dimethylamine yielded N,N-dimethyl-γ-cycloöctatetraenyl-*n*-propylamine (IV) (54%), while with potassium cyanide γ-cycloöctatetraenyl-*n*-propyl cyanide (V) (74%) was formed, identical in properties with V prepared by copolymerization. Reduction of the cyanide V with lithium aluminum hydride yielded δ-cycloöctatetraenyl-*n*-butylamine (VI) (39%), and saponification of V yielded γ-cycloöctatetraenyl-*n*-butyric acid (VII) (69%). The acid VII was isolated as a yellow liquid that formed a crystalline salt with quinine. After recrystallization of the salt to constant melting point and optical rotation, the acid was regenerated by treatment with 1% hydrochloric acid at 0°, and proved to be optically inactive.

Reactions that were used successfully in the course of this work to modify the side chains of substituted cycloöctatetraenes that had not been demonstrated previously to be applicable without disruption of the cycloöctatetraene ring included the following: oxidation of a primary alcohol to an acid with chromic acid; oxidation of a secondary alcohol to a ketone with chromic acid or by the Oppenauer method; sodium hypobromite oxidation of a methylcarbinol to an acid; Grignard synthesis of a tertiary alcohol from a carboxylic ester. Types of functionally substituted acetylenes that were used successfully for the first time in the preparation of substituted cycloöctatetraenes by copolymerization with acetylene were an acetylenic ketone and an acetylenic nitrile.

Experimental[4]

Procedures that have been described previously for the copolymerization of substituted acetylenes with acetylene

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

(2) A. C. Cope and D. F. Rugen, THIS JOURNAL, **75**, 3215 (1953).

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

(4) 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.

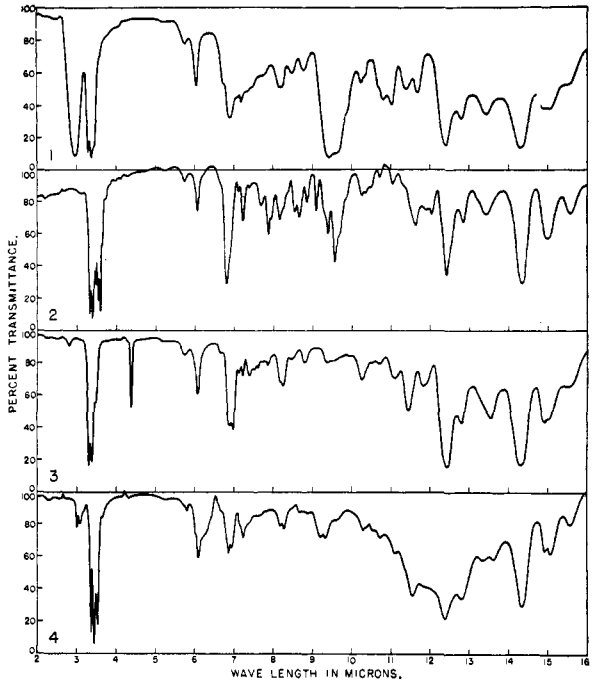


Fig. 1.—Infrared absorption spectra: curve 1, γ-cyclooctatetraenyl-*n*-propyl alcohol (I); curve 2, N,N-dimethyl-γ-cycloöctatetraenyl-*n*-propylamine (IV); curve 3, γ-cycloöctatetraenyl-*n*-propyl cyanide (V); curve 4, δ-cycloöctatetraenyl-*n*-butylamine (VI). The spectra were determined without solvent in a 0.025-mm. cell.

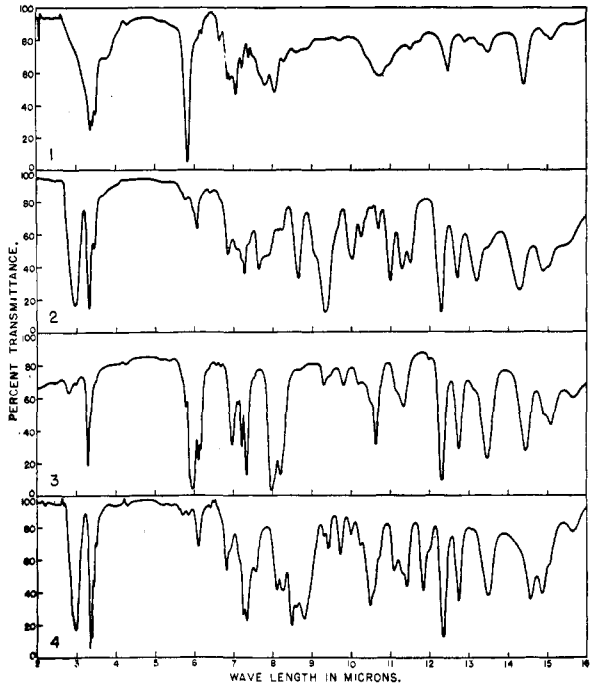


Fig. 2.—Infrared absorption spectra: curve 1, γ-cyclooctatetraenyl-*n*-butyric acid (VII); curve 2, cycloöctatetraenylmethylcarbinol (VIII); curve 3, cycloöctatetraenyl methyl ketone (IX); curve 4, cycloöctatetraenyldimethylcarbinol (XI). Curve 1 was determined with solutions (100 mg./ml.) in carbon tetrachloride in the region 2–8μ and in carbon disulfide in the region 8–16μ in a 0.10-mm. cell. Curves 2–4 were determined without solvent in a 0.025-mm. cell.

and purification of the resulting substituted cycloöctatetraenes by chromatography on silica gel were used.[2]

γ-Cycloöctatetraenyl-*n*-propyl Alcohol (I).—4-Pentyn-1-ol was prepared from 120.5 g. of tetrahydrofurfuryl chloride and sodamide in liquid ammonia in a yield of 65.5 g. (78%), b.p. 70–71° (29 mm.), $n^{25}D$ 1.4443.[5] Copolymerization of 20 g. of 4-pentyn-1-ol with acetylene by the general procedure described previously[2] resulted in an absorption of 1200 p.s.i. of acetylene and an increase in weight of 171 g. in 8 hours at 84–92°. After purification by chromatography on silica gel[2] and fractionation through a semimicro column, the yield of the pure alcohol I was 3.5 g. (8%), b.p. 91–91.5° (0.15 mm.), $n^{25}D$ 1.5426, d^{25}_4 1.0244.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.48; H, 8.64. Found: C, 81.36; H, 8.85.

β-Cycloöctatetraenylpropionic acid (II) was obtained by treating a solution of 0.50 g. of the alcohol I in 40 ml. of acetone (distilled from potassium permanganate) with 8 ml. of a solution prepared from 23.3 g. of chromium trioxide, 19.7 ml. of concentrated sulfuric acid and 50 ml. of water.[6] The oxidizing agent was added dropwise with stirring and cooling to keep the reaction temperature below 25°, and the mixture was allowed to stand for 30 minutes. Water (40 ml.) was added and the mixture was extracted thoroughly with ether. The extracts were combined, washed with water, and extracted with 10% sodium hydroxide solution. The alkaline extracts were acidified with hydrochloric acid and re-extracted with ether. The extracts were dried over sodium sulfate, concentrated under reduced pressure after addition of benzene, and the yellow acid II that crystallized from the residue on cooling was recrystallized from hexane; yield 0.22 g. (37%), m.p. and mixed m.p. with an authentic sample,[2] 58.8–59.8°.

γ-Cycloöctatetraenyl-*n*-propyl *p*-Toluenesulfonate (III).—A solution of 4.0 g. of the alcohol I in 6 ml. of pyridine was cooled in an ice-bath, and 6.87 g. of *p*-toluenesulfonyl chloride was added in one portion. The mixture was allowed to stand in the ice-bath for 3.5 hours, with frequent agitation by swirling. Water (20 ml.) was added, and after 30 minutes the mixture was extracted twice with ether, and the extracts were washed with 10% hydrochloric acid, sodium bicarbonate solution and water. The ether solution was dried over magnesium sulfate, concentrated under reduced pressure, and the liquid residue of the crude *p*-toluenesulfonate III was evacuated at 16 mm. and room temperature for 15 minutes; yield 7.47 g. (96%).

N,N-Dimethyl-γ-cycloöctatetraenyl-*n*-propylamine (IV).—A solution of 3.0 g. of the *p*-toluenesulfonate III in 15 ml. of benzene was saturated with dimethylamine and allowed to stand overnight at room temperature. Ether (20 ml.) was added, and the solution was washed with water and dried over magnesium sulfate. Concentration of the solution and fractionation of the residue through a semimicro column yielded 0.98 g. (54%) of the amine IV, b.p. 50–55° (0.01 mm.), $n^{25}D$ 1.5158–1.5164. An analytical sample had b.p. 55° (0.01 mm.), $n^{25}D$ 1.5164, d^{25}_4 0.9234.

Anal. Calcd. for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.47; H, 10.07; N, 7.17.

N,N-Dimethyl-γ-cycloöctatetraenyl-*n*-propylamine picrate was prepared by adding the amine IV to a saturated solution of picric acid in ether and recrystallized to a constant melting point of 103.5–104° from 95% ethanol.

Anal. Calcd. for $C_{19}H_{22}N_4O_7$: C, 54.53; H, 5.30; N, 13.39. Found: C, 54.23; H, 5.35; N, 13.55.

γ-Cycloöctatetraenyl-*n*-propyl Cyanide (V). (a).—A solution of 1.82 g. of the *p*-toluenesulfonate III and 0.75 g. of potassium cyanide in 10 ml. of 80% ethanol was heated under reflux on a steam-bath for 2 hours. The solution was poured into 25 ml. of water and extracted with ether. The ether extracts were dried over magnesium sulfate, concentrated, and the residue was fractionated through a semimicro column, yielding 0.73 g. (74%) of the nitrile V, b.p. 95–103.5° (1 mm.), $n^{25}D$ 1.5263–1.5290. A redistilled analytical sample had b.p. 103.5–104.5° (0.5 mm.), $n^{25}D$ 1.5300, d^{25}_4 0.9911.

(5) G. Eglinton, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, 2873 (1952).

(6) Based on an oxidation procedure described by R. G. Curtis, I. Heilbron, E. R. H. Jones and G. F. Woods, *J. Chem. Soc.*, 461 (1953).

Anal. Calcd. for $C_{12}H_{13}N$: C, 84.21; H, 7.60; N, 8.19. Found: C, 84.27; H, 7.81; N, 8.06.

(b).—The nitrile V also was prepared by the copolymerization of 10 g. of 5-hexynenitrile (b.p. 64–65° at 10 mm., $n^{25}D$ 1.4389, prepared from 4-pentyn-1-yl *p*-toluenesulfonate and sodium cyanide[7]) with acetylene at 86–93°, with acetylene absorption of 1020 p.s.i. (134 g.) in 11 hours, and purified by chromatography on silica gel. The yield of V with physical properties and infrared spectrum identical within experimental error with the sample described above that was prepared from the *p*-toluenesulfonate III was 2.1 g. (11%).

δ-Cycloöctatetraenyl-*n*-butylamine (VI).—A solution of 1.23 g. of the nitrile V in 15 ml. of dry ether was added slowly with stirring to 0.31 g. of lithium aluminum hydride in 20 ml. of ether in a nitrogen atmosphere. The mixture was heated under reflux for 1 hour, cooled and 5 ml. of water was added cautiously, followed by 35 ml. of 10% hydrochloric acid. After extraction with ether (extracts discarded), the solution was made basic with 10% sodium hydroxide and re-extracted with ether. The extracts were dried over magnesium sulfate, concentrated, and the residue was distilled through a semimicro column, yielding 0.49 g. (39%) of the amine VI, b.p. 82–83° (0.7 mm.), $n^{25}D$ 1.5330–1.5334. An analytical sample had b.p. 83° (0.7 mm.), $n^{25}D$ 1.5334, d^{25}_4 0.9535.

Anal. Calcd. for $C_{12}H_{17}N$: C, 82.31; H, 9.71; N, 8.00. Found: C, 82.16; H, 9.92; N, 7.90.

δ-Cycloöctatetraenyl-*n*-butylamine hydrochloride was prepared by passing hydrogen chloride into a solution of 0.246 g. of the amine VI in 10 ml. of dry ether. The hydrochloride was obtained in a yield of 0.184 g. (59%) after recrystallization from methanol–ether to a constant melting point of 110.5–111.5°.

Anal. Calcd. for $C_{12}H_{18}ClN$: C, 68.07; H, 8.57; N, 6.62. Found: C, 68.05; H, 8.72; N, 6.63.

γ-Cycloöctatetraenyl-*n*-butyric Acid (VII).—The nitrile V (1.9 g.) was heated under reflux for 12 hours with a solution of 3.0 g. of sodium hydroxide in 50 ml. of water. The solution was cooled, extracted with ether (extracts discarded) and acidified with 10% hydrochloric acid. The acid VII was extracted with three 20-ml. portions of ether, which were dried over magnesium sulfate and concentrated. Fractionation of the residue through a semimicro column yielded 1.45 g. (69%) of the acid VII, b.p. 95–97° (0.019 mm.), $n^{25}D$ 1.5310. The acid failed to crystallize.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.77; H, 7.41. Found: C, 75.25; H, 7.45.

The quinine salt of γ-cycloöctatetraenyl-*n*-butyric acid was prepared by adding a solution of 0.15 g. of the acid VII in 1 ml. of ether to a solution of 0.299 g. of quinine hydrate in 50 ml. of ether. The solution was concentrated to 10 ml. and cooled overnight at 5°. The light yellow crystalline salt (0.325 g., 80%) was crystallized twice from ether to a constant melting point of 101–102°, $[\alpha]^{27}D$ −114.8° (l = 1, c 0.95 in absolute ethanol).

Anal. Calcd. for $C_{32}H_{38}N_2O_4$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.45; H, 7.56; N, 5.56.

The acid VII that was regenerated from the quinine salt with 1% hydrochloric acid at 0° and immediately extracted with carbon tetrachloride was optically inactive.

Cycloöctatetraenylmethylcarbinol (VIII).—3-Butyn-2-ol (20 g., Farchan Research Laboratories) was copolymerized with acetylene by the general procedure described previously.[2] Acetylene absorption amounted to 1080 p.s.i., with a weight increase of 102 g. during 10.5 hours at 84–90°. Separation of the products by the usual procedure, including chromatography on silica gel, yielded 36 g. of cyclooctatetraene and 4.56 g. (11%) of the alcohol VIII (eluted from the silica gel with ether); b.p. 80–85° (0.9 mm.), $n^{25}D$ 1.5455–1.5472. A redistilled analytical sample had b.p. 70° (0.4 mm.), $n^{25}D$ 1.5460, d^{25}_4 1.0385.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 81.04; H, 8.10. Found: C, 81.10; H, 8.16.

Cycloöctatetraenecarboxylic acid was obtained by adding 0.50 g. of the alcohol VIII dropwise with stirring at a temperature below 10° to the sodium hypobromite prepared from 1.9 g. of sodium hydroxide in 16 ml. of water and 2.42 g. of bromine. The mixture was stirred at room temperature for 12 hours, extracted with ether (extracts discarded), acidified with 6 *N* sulfuric acid, and re-extracted with ether. The extracts were washed with water, dried over sodium sulfate and concentrated under reduced pressure. Sublimation of the residue by heating at 0.5 mm. yielded 0.183 g. (37%) of cycloöctatetraenecarboxylic acid, m.p. 69–73°, which after recrystallization from ether had m.p. and mixed m.p. with an authentic sample[3] of 71.5–72.8°.

Cycloöctatetraenyl Methyl Ketone (IX). (a).—To a solution of 3.5 g. of the carbinol VIII in 20 ml. of acetone was added dropwise with stirring at 0° and in a nitrogen atmosphere during 25 minutes a solution of 1.43 g. of chromium trioxide and 1.5 ml. of sulfuric acid in 5 ml. of water. After the addition was completed, the mixture was stirred for 2.5 hours at 0° and poured into 100 ml. of ice-water. The mixture was extracted with ether, and the extracts were washed with water and dried over sodium sulfate. Concentration and distillation of the residue through a semimicro column yielded 1.69 g. (53%) of the ketone IX, b.p. 65–68.5° (0.55 mm.), $n^{25}D$ 1.5470–1.5518, which was purified through the oxime.

Cycloöctatetraenyl methyl ketoxime (X) was prepared by heating a solution of 0.35 g. of the ketone IX and 0.17 g. of hydroxylamine hydrochloride in 5 ml. of pyridine and 5 ml. of absolute ethanol on a steam-bath under reflux for 15 hours. The solution was concentrated and water was added to the crystalline residue, which was collected on a filter and washed with water. The yield of the oxime was 0.33 g. (85%) after recrystallization from methanol; m.p. 150–151°.

Anal. Calcd. for $C_{10}H_{11}NO$: C, 74.53; H, 6.83; N, 8.70. Found: C, 74.35; H, 6.89; N, 8.48.

The ketone IX was regenerated from 0.60 g. of the oxime, which was heated under reflux for 3.5 hours with 0.78 g. of pyruvic acid and 0.38 g. of sodium acetate in 5 ml. of acetic acid and 2 ml. of water.[8] The solution was poured into 20 ml. of water and extracted with two 20-ml. portions of ether. The extracts were washed with saturated sodium bicarbonate solution, water, dried over sodium sulfate and concentrated. Benzene was added and distilled under reduced pressure to complete removal of the water, and the residue was fractionated through a semimicro column. The yield of IX was 0.31 g. (57%), b.p. 73–74° (1.2 mm.), $n^{25}D$ 1.5519–1.5549. A redistilled analytical sample had b.p. 74° (1.2 mm.), $n^{25}D$ 1.5548, d^{25}_4 1.0319. A number of analyses of several samples of the ketone were slightly low in carbon, but it is believed to be pure because the physical properties (including infrared spectra) of the samples regenerated under nitrogen from the analytically pure ketoxime X were identical.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.20; H, 6.90. Found: C, 81.43; H, 6.98.

The ketone IX also was prepared in poorer (18–30%) yield by Oppenauer oxidation of the carbinol VIII with acetone and aluminum *t*-butoxide in benzene.

Cycloöctatetraenyl methyl ketone 2,4-dinitrophenylhydrazone was prepared by adding a solution of the ketone in 95% ethanol at room temperature to a slight excess of a solution prepared from 0.4 g. of 2,4-dinitrophenylhydrazine, 2 ml. of concentrated sulfuric acid, 3 ml. of water and 10 ml. of 95% ethanol. The derivative was recrystallized from a mixture of ethanol and ethyl acetate; m.p. 202–203° (dec.).

Anal. Calcd. for $C_{16}H_{14}N_4O_4$: C, 58.89; H, 4.33; N, 17.18. Found: C, 58.72; H, 4.50; N, 16.98.

(b).—Copolymerization of 19 g. of 3-butyn-2-one[9] with acetylene resulted in the absorption of 1160 p.s.i. (117 g.) of acetylene in 11 hours at 85–90°. Purification of the product by the general procedure described previously, including chromatography on silica gel, yielded 28.5 g. of cycloöctatetraene and 0.60 g. (1.5%) of IX, b.p. 85–90° (1 mm.), identified by m.p. and mixed m.p. of the 2,4-dinitrophenylhydrazone with the derivative described above (201–202° dec.).

Cycloöctatetraenyldimethylcarbinol (XI).—Copolymerization of 20 g. of 2-methyl-3-butyn-2-ol (Farchan Research Laboratories) with acetylene resulted in the absorption of 1030 p.s.i. of acetylene (153 g.) in 8.5 hours at 85–88°.

(7) G. Eglinton, Doctoral Thesis, University of Manchester, 1951; G. Eglinton, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, to be published.

(8) Based on a procedure described by E. B. Hershberg, *J. Org. Chem.*, **13**, 542 (1948).

(9) E. R. H. Jones, K. Bowden, I. M. Heilbron and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

Purification by the usual procedure,[2] including chromatography on silica gel, yielded 37 g. of cycloöctatetraene and 5.0 g. (13%) of the carbinol XI, b.p. 73–75.5° (0.5 mm.), $n^{25}D$ 1.5370–1.5382. A redistilled analytical sample had b.p. 74.5–75.5° (1.3 mm.), $n^{25}D$ 1.5370, d^{25}_4 1.1024.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.48; H, 8.64. Found: C, 81.49; H, 8.79.

An authentic sample of the carbinol XI was prepared by adding methyl cycloöctatetraenecarboxylate[3] (1.28 g.) in 10 ml. of dry ether to the methylmagnesium iodide prepared from 0.36 g. of magnesium and 2.27 g. of methyl iodide in 20 ml. of dry ether. The magnesium salts were decomposed with aqueous ammonium chloride and the ether solution was washed with water, dried over magnesium sulfate and concentrated. Distillation of the residue through a semimicro column yielded 0.81 g. of crude XI, b.p. 73–75° (2.5 mm.), $n^{25}D$ 1.5369–1.5371. The infrared spectrum of the product showed a strong carbonyl band, so it was purified by chromatography on a column containing 25 g. of neutral alumina with activity 3.[10] Elution with 300 ml. of benzene followed by concentration and distillation yielded 0.49 g. of recovered methyl cycloöctatetraenecarboxylate, b.p. 76° (2.3 mm.), $n^{25}D$ 1.5371, identified by the infrared spectrum. Elution with 300 ml. of ether followed by concentration and distillation through a semimicro column yielded 0.21 g. of XI, b.p. 74.5° (3.0 mm.), $n^{25}D$ 1.5357, which had an infrared spectrum identical with XI prepared by copolymerization, except for the presence of weak bands at 5.83 and 6.5 μ due to a small amount of impurity.

(10) H. Brockman and H. Schodder, *Ber.*, **74**, 73 (1945).

CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Polynuclear Aromatic Hydrocarbons. I. A New Synthesis of Picene

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9,10-Dihydrophenanthrene (I) has been found to be a suitable intermediate in a new synthesis of picene. The synthetic scheme, which is considerably shorter than those heretofore reported, depends on the diacylation of I to give the symmetrical diketoester, II, which may be reduced, dehydrogenated and preferentially cyclized to XI, a compound readily convertible to picene, XII. The over-all yield for the synthesis is 7.5%.

Among the dehydrogenation products of pentacyclic triterpenoids are found the substituted picenes. When the structure of these picenes is known, the position of the methyl groups in the extreme rings of the triterpene may usually be determined. An example is the conversion of β-amyrin to 2,9-dimethylpicene.[1] Consequently, it is of some value to devise a synthesis of this ring system which is particularly adaptable to the preparation of picenes encountered in triterpenoid degradations. Such a synthesis forms the basis for the present communication.

The difficulties and potential ambiguities in the recorded preparations of picene derivatives have already been reported by Newman.[2,3] The latter author avoided the use of an intramolecular cyclization catalyzed by aluminum chloride in view of the known lability of alkyl groups under these conditions.[4] However, as many as fifteen steps were still required for the preparation of 2,9-dimethylpicene which resulted in an over-all yield of approximately 0.1%.[3]

It appeared likely that a suitable phenanthrene derivative might serve as a starting material for a shorter synthesis. In this paper we report the successful synthesis of picene (see Charts 1 and 2) from 9,10-dihydrophenanthrene.

It has been found possible to diacylate I by using β-carbomethoxypropionyl chloride and a large excess of aluminum chloride. In this way a 48% yield of diketoester II has been obtained, accompanied by a 36% yield of the expected monoacylated product, VI. Assignment of the second acyl group to the 7-position in II is in accord with the results of Mosettig and Stuart[5] who found that 2-hydroxy-9,10-dihydrophenanthrene gave rise to 7-acyl derivatives when treated with various acid chlorides in the presence of aluminum chloride. These findings are to be expected in view of the well-known tendency of the structurally analogous biphenyl to acylate in the p,p'-positions.[6,7]

Succinoylation of 9,10-dihydrophenanthrene (I) using succinic anhydride in place of the acid chloride gave quantitative yields of the monoacylated product, V, but a large excess of aluminum chloride failed to produce any diacylated compound corresponding to II. Wolff–Kishner reduction of V or VI followed by esterification gave VII and acylation of this ester with β-carbomethoxypropionyl chloride resulted in VIII. Reduction of *either* II *or* VIII gave III.

Although acid III could be dehydrogenated directly to IX by heating with a 10% palladium–charcoal catalyst, much more satisfactory results were obtained by using the ester, IV, followed by hydrolysis to IX.

It was found possible to cyclize acid IX under a variety of conditions, all of which resulted in a mixture of diketones that included XI as the predominant isomer. Yields of ketone XI were highest when polyphosphoric acid[8] was used although stannic chloride gave similar results. A double ring closure of this type has not been previously reported in the phenanthrene series although preferred cyclization as indicated in the conversion of IX to XI could be predicted on the basis of results obtained with monosubstituted phenanthrenes. Thus the acids XIII[9a]

(1) L. Ruzicka, E. Schellenberg and M. W. Goldberg, *Helv. Chim. Acta*, **20**, 791 (1937).

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