layer with two additional 10-ml. portions of water, the combined aqueous layers were acidified with hydrochloric acid. The colorless crystalline acid was extracted with ether, and the extracts were dried over magnesium sulfate and concentrated, yielding 2.2 g. of cycloöctene-1-carboxylic acid as a white solid, m.p. 98.6–101.6°. Recrystallization from ether yielded 1.40 g. (30%) of the acid, m.p. 101.8–102.6°. This sample of the acid was identical with the sample prepared from cycloöctatetraenecarboxylic acid (mixed melting point and comparison of the infrared spectra). The ultraviolet spectrum (Fig. 1, curve 2), determined in 95% ethanol with a Beckman model DU quartz ultraviolet spectrophotometer, also was identical with the spectrum of the acid derived from cycloöctatetraenecarboxylic acid and contained a maximum at 218 mμ (ε 12,100). This maximum may be compared with the maximum at 212 mμ (ε 11,000) reported for cyclohexene-1-carboxylic acid.[8]

Hydrogenation of a solution of 0.444 g. of cycloöctene-1-carboxylic acid (prepared from 1-cycloöctenyllithium) in 4 ml. of glacial acetic acid in the presence of 0.1 g. of prereduced platinum oxide was complete in 3 hours and resulted in absorbtion of 101% of one molar equivalent of hydrogen. The cycloöctanecarboxylic acid formed was isolated by the procedure described above; 0.35 g. (78%), b.p. 90–92° (0.10 mm.), $n^{25}\text{D}$ 1.4782, and had an infrared spectrum identical with the authentic sample.[12]

Methyl Cycloöctatetraenecarboxylate.—An ethereal solution (25 ml.) containing the diazomethane prepared from 2.0 g. of nitrosomethylurea was added to a solution of 1.0 g. of cycloöctatetraenecarboxylic acid in 20 ml. of ether. After nitrogen evolution ceased, glacial acetic acid was added dropwise to decompose the excess diazomethane, and the solution was washed with two 10-ml. portions of saturated sodium bicarbonate solution and dried over magnesium sulfate. After concentration, the residue was distilled through a semi-micro column, and yielded 0.976 g. (89%) of methyl cycloöctatetraenecarboxylate as a yellow liquid, b.p. 75–76.2° (5 mm.), $n^{25}\text{D}$ 1.5398, d^{25}_4 1.092.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.23; sapn. equiv., 162. Found: C, 74.06; H, 6.42; sapn. equiv., 161.

Saponification of 0.105 g. of the ester with very dilute aqueous sodium hydroxide containing a little ethanol at about 80° for 2 hours yielded 0.078 g. (81%) of cycloöctatetraenecarboxylic acid, m.p. and mixed m.p. 72–73°.

Quinine Salt of Cycloöctatetraenecarboxylic Acid.—A solution of 1.00 g. of cycloöctatetraenecarboxylic acid in 100 ml. of ether was added to 2.6 g. of quinine hydrate in 200 ml. of ether. The yellow, crystalline salt which separated slowly weighed 2.89 g. (91%) after drying. The salt melted at 200.6–202° (dec.) and had $[\alpha]^{28°}\text{D}$ −122.5° (l. = 1, *c* 2.0 in 95% ethanol). After one recrystallization from ethyl acetate and three from water, these physical constants were unchanged.

Anal. Calcd. for $C_{29}H_{32}N_2O_4$: C, 73.55; H, 7.02; N, 5.92. Found: C, 73.57; H, 6.94; N, 6.00.

l-β-Phenylisopropylamine Salt of Cycloöctatetraenecarboxylic Acid.—A solution of l-β-phenylisopropylamine was prepared by neutralizing 1.88 g. of the sulfate with 0.64 g. of sodium hydroxide in 50 ml. of water and extracting the base with 50 ml. of ether. This solution was added to 1.00 g. of cycloöctatetraenecarboxylic acid in 25 ml. of ether. Yellow needles of the salt separated slowly, which after drying weighed 1.85 g. (97%); m.p. 155.6–157.2°, $[\alpha]^{28}\text{D}$ +1.4° (l. = 1, *c* 2.0 in 95% ethanol). After two recrystallizations from ethyl acetate and two from water, the melting point and rotation were unchanged.

Anal. Calcd. for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47; N, 4.94. Found: C, 76.06; H, 7.44; N, 4.98.

d-β-**Phenylisopropylamine Salt of Cycloöctatetraenecarboxylic Acid.**—This salt was prepared by the procedure described for the salt of the *l*-base in a yield of 1.73 g., m.p. 155.9–157.2°, $[\alpha]^{28}\text{D}$ −0.5° (l. = 1, *c* 2.0 in 95% ethanol). Three crystallizations from ethyl acetate and two from water did not change these physical constants.

Anal. Calcd. for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47; N, 4.94. Found: C, 76.29; H, 7.42; N, 4.92.

CAMBRIDGE, MASS. RECEIVED JUNE 14, 1951

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

Cyclic Polyolefins. XXI. Alkylcycloöctatetraenes and Alkylcycloöctatrienes from Cycloöctatetraene and Alkyllithium Compounds

BY ARTHUR C. COPE AND HARRIS O. VAN ORDEN[1]

The reaction of typical *n*-alkyllithium compounds (ethyllithium and *n*-butyllithium) with cycloöctatetraene in ether proceeds by addition, followed by the equivalent of lithium hydride transfer to another molecule of cycloöctatetraene. The products formed are the *n*-alkylcycloöctatetraenes and a mixture of 1,3,5- and 1,3,6-cycloöctatrienes, plus small amounts of the alkylcycloöctatrienes. Reaction of *n*-butyllithium and *s*-butyllithium with cycloöctatetraene in pentane results only in addition, and yields the alkylcycloöctatrienes.

This paper reports an extension of the preparation of arylcycloöctatetraenes from cycloöctatetraene and aryllithium compounds[2] to the synthesis of alkylcycloöctatetraenes. *n*-Butyllithium and ethyllithium were investigated as typical *n*-alkyllithium derivatives. Both reacted with cycloöctatetraene in ether, and after hydrolysis the hydrocarbons isolated were the alkylcycloöctatetraenes (I and II), alkylcycloöctatrienes (III and IV), a mixture of 1,3,5- and 1,3,6-cycloöctatrienes (V) and recovered cycloöctatetraene. The mixtures were separated by a combination of fractional distillation and differential extraction with silver nitrate. The reactions presumably follow the same course as the reaction of cycloöctatetraene with aryllithium compounds, which formed similar products.[2]

The hydrocarbons formed from *n*-butyllithium were separated by an initial differential extraction with aqueous silver nitrate. Extraction with 20–25% silver nitrate separated recovered cycloöctatetraene (38%), while 50% silver nitrate extracted *n*-butylcycloöctatetraene and the isomeric cycloöctatrienes (V). After regeneration of the hydrocarbons from the 50% silver nitrate extract by treatment with an excess of sodium chloride, fractional distillation separated *n*-butylcycloöctatetraene (14.5%) from the cycloöctatrienes (11.5%). A small amount (3%) of *n*-butylcycloöctatriene (III) was isolated by distillation of the fraction that was insoluble in aqueous silver nitrate.

The products formed from ethyllithium were separated by the more advantageous procedure of an initial distillation to separate (1) a mixture of cycloöctatetraene and cycloöctatrienes from (2) a mixture of ethylcycloöctatetraene and ethylcyclo-

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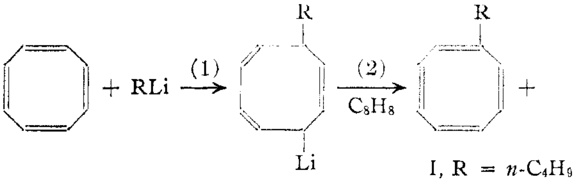
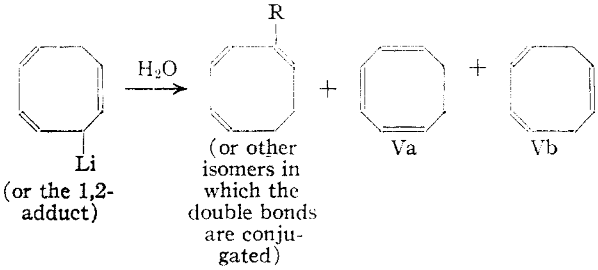
[1] du Pont Fellow, 1949–1950.

[2] A. C. Cope and M. R. Kinter, THIS JOURNAL, **72**, 630 (1950); **73**, 3424 (1951).



(or the 1,2-adduct)

I, R = n-C_4H_9
II, R = C_2H_5



III, R = n-C_4H_9
IV, R = C_2H_5
VIII, R = s-C_4H_9

octatriene. Extraction of each of these mixtures with 20% silver nitrate separated the cycloöctatetraene and ethylcycloöctatetraene as water-soluble silver nitrate complexes; the yields (after regeneration of the ethylcycloöctatetraene from its silver nitrate complex by treatment with ammonium hydroxide) were: ethylcycloöctatetraene, 29%; ethylcycloöctatriene, 5%; cycloöctatrienes, 31%.

Ethylcycloöctatetraene and n-butylcycloöctatetraene were yellow liquids which were characterized by ultraviolet (Fig. 1) and infrared absorption spectra (Fig. 2), and by quantitative hydrogenations which resulted in the absorption of 99 and 100% of four molar equivalents of hydrogen. The reduction product of ethylcycloöctatetraene was identified as ethylcycloöctane by comparison of its infrared spectrum with the spectrum of an authentic sample described previously.[3] n-Butylcycloöctane formed by the reduction of I was identified by comparison of its infrared spectrum with the spectrum of a sample prepared from cycloöctanone and n-butylmagnesium bromide, by dehydration of the intermediate alcohol to n-butylcycloöctene (VI), followed by hydrogenation to n-butylcycloöctane (VII).

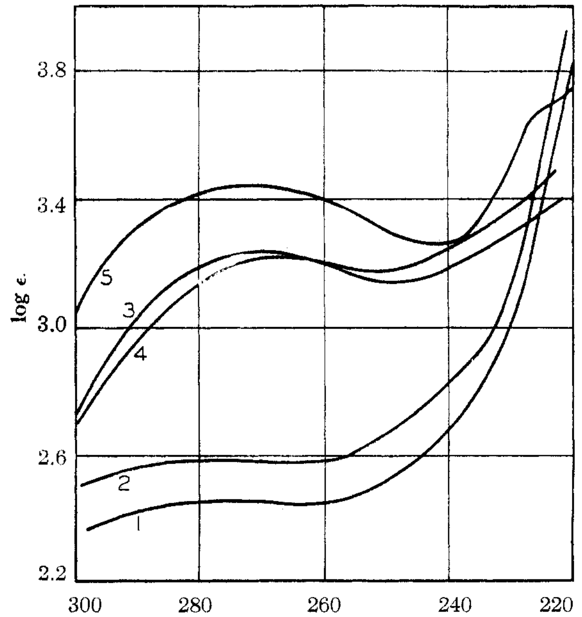


Fig. 1.—Ultraviolet absorption spectra: curve 1, ethylcycloöctatetraene (IV); curve 2, n-butylcycloöctatetraene (III); curve 3, s-butylcycloöctatriene (VIII); curve 4, n-butylcycloöctatriene (III); curve 5, ethylcycloöctatriene (IV), all determined in purified cyclohexane with a Beckman model DU quartz spectrophotometer.

VI, R = n-C_4H_9
IX, R = s-C_4H_9

VII, R = n-C_4H_9
X, R = s-C_4H_9

The ethyl and n-butylcycloöctatrienes formed in small amounts from cycloöctatetraene and the corresponding organolithium compounds in ether also were characterized by quantitative hydrogenations, which resulted in absorption of 88.5 and 93.8% of three molar equivalents of hydrogen and yielded the corresponding alkylcycloöctanes, identified by their infrared spectra. The mixture of cycloöctatriene isomers (Va and Vb) was identified by its ultraviolet absorption spectrum, by isomerization with potassium t-butoxide to 1,3,5-cycloöctatriene (Va), and by preparation of the crystalline

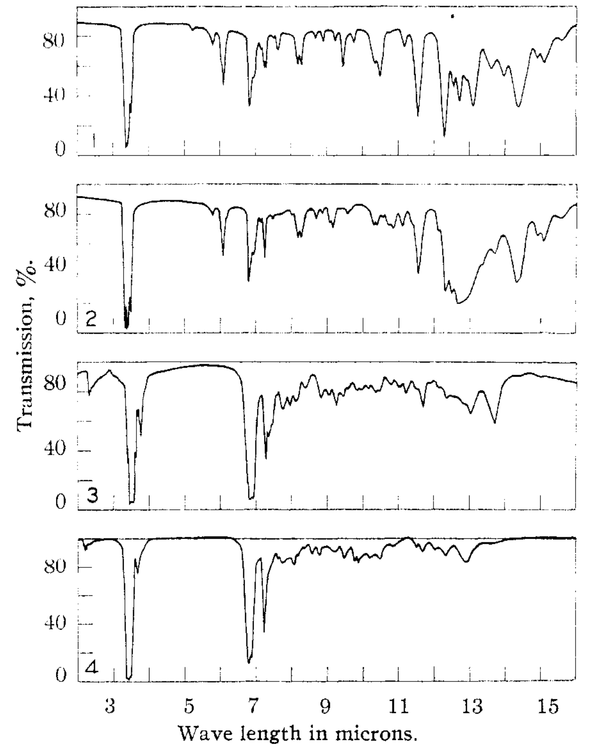


Fig. 2.—Infrared absorption spectra: curve 1, ethylcycloöctatetraene (IV); curve 2, n-butylcycloöctatetraene (III); curve 3, n-butylcycloöctane (VII), sample prepared by reduction of III; curve 4, s-butylcycloöctane (X), sample prepared from cycloöctanone. The spectra were determined for the pure liquids with a cell thickness of 0.025 mm.

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[3] A. C. Cope and S. W. Fenton, THIS JOURNAL, **73**, 1195 (1951).

maleic anhydride adduct and silver nitrate complex of Va.[4]

Preliminary attempts to prepare methylcycloöctatetraene or methylcycloöctatriene by the reaction of methyllithuim with cycloöctatetraene in ether resulted in no apparent reaction, and recovery of the cycloöctatetraene. Methyllithium is known to be less reactive than other alkyllithium derivatives.[5] *Secondary* alkyllithium compounds, on the other hand, are so reactive that they are commonly prepared in pentane because of the rapidity with which they cleave ether.[6] *s*-Butyllithium and cycloöctatetraene reacted exothermically in pentane, but the product isolated after hydrolysis of the intermediate lithium derivative was the colorless *s*-butylcycloöctatriene (VIII, 32%), rather than *s*-butylcycloöctatetraene. In order to determine whether this difference in behavior compared to *n*-alkyllithium compounds studied previously was characteristic of the *s*-alkyllithium derivative, *n*-butyllithium was prepared and treated with cycloöctatetraene in pentane; the product was *n*-butylcycloöctatriene (III, 18%). Accordingly the reaction of alkyllithium derivatives with cycloöctatetraene in pentane provides a route to alkylcycloöctatrienes, while in ether an oxidation–reduction reaction with a second mole of cycloöctatetraene occurs and the principal products are the alkylcycloöctatetraenes. The alkylcycloöctatrienes prepared from organolithium compounds and cycloöctatetraene are undoubtedly mixtures of isomers, but their three double bonds are conjugated, at least to a large extent, according to the maxima observed in their ultraviolet spectra (Fig. 1).

s-Butylcycloöctatriene was identified by quantitative hydrogenation, which resulted in absorption of 91.3% of three molar equivalents of hydrogen and formed *s*-butylcycloöctane. An authentic sample of *s*-butylcycloöctane was prepared for comparison by treating cycloöctanone with *s*-butyllithium to form 1-*s*-butylcycloöctanol, dehydrating the alcohol to *s*-butylcycloöctene (IX), and hydrogenating the olefin to *s*-butylcycloöctane (X). The infrared spectra of the two samples of X were identical within experimental error.

Experimental[7]

Reaction of Cycloöctatetraene with *n*-Butyllithium in Ether.—A solution of *n*-butyllithium[8] was prepared from 54.8 g. of *n*-butyl bromide and 5.6 g. of lithium wire in 160 ml. of dry ether, and 83.3 g. of cycloöctatetraene[9] was added slowly with stirring during 50 minutes at 0–20°. The mixture was stirred at room temperature for 30 minutes, heated under reflux for 5 hours, and then cooled in ice. Cold water was added slowly, and the ether layer was separated and combined with five 30- to 50-ml. ether extracts of the aqueous layer. The ether solution was washed with four portions of cold water and then was extracted with (1) twelve 25-ml. portions of 20% aqueous silver nitrate; (2) three 25-ml. portions of 50% silver nitrate (in each of these extractions 25 ml. of water was added to dissolve the solid cycloöctatetraene–silver nitrate complex that separated); (3) fourteen 25-ml. portions of 50% silver nitrate. Each of the silver nitrate extracts was treated with an excess of saturated sodium chloride solution, and the hydrocarbons which were liberated were extracted with ether. The ether solutions were dried over magnesium sulfate and distilled through a semi-micro column.[10] Extract (1) yielded 19.2 g. (23%) of recovered cycloöctatetraene, b.p. 70° (90 mm.), n^{25}D 1.5339–1.5341. Extract (2) yielded 12.3 g. (15%) of recovered cycloöctatetraene and 0.18 g. of *n*-butylcycloöctatetraene (I) (described below), b.p. 98° (20 mm.), n^{25}D 1.5085.

***n*-Butylcycloöctatetraene (I)** was isolated from the hydrocarbons regenerated from extract (3), which were separated by fractional distillation into a mixture of cycloöctatrienes containing some cycloöctatetraene (described below, 11.5 g., b.p. 45° at 20 mm., n^{25}D 1.5142–1.5148) and 9.3 g. (14.5%) of I, b. p. 98° (20 mm.), n^{25}D 1.5085. A redistilled analytical sample of this yellow hydrocarbon had b.p. 98° (20 mm.), n^{25}D 1.5083, d^{25}_{4} 0.8876.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.98; H, 10.09.

Hydrogenation of a solution of 1.53 g. of I in 25 ml. of glacial acetic acid in the presence of 0.15 g. of prereduced platinum oxide was complete in 3 hours, and 100% of four molar equivalents of hydrogen was absorbed. The catalyst was separated, sodium hydroxide was added with cooling to neutralize the acetic acid, and the product was extracted with five small portions of ether. The extracts were dried over magnesium sulfate and distilled, yielding 0.98 g. of *n*-butylcycloöctane, b.p. 92.5–93° (8 mm.), n^{25}D 1.4592, which was proved to be identical with an authentic sample described below by correspondence in physical properties, including the infrared spectrum (Fig. 2).

Anal. Calcd. for $C_{12}H_{24}$: C, 85.64; H, 14.36. Found: C, 85.90; H, 14.43.

***n*-Butylcycloöctatriene (III)** was obtained from the ether solution containing hydrocarbons which were not removed by any of the extractions with silver nitrate, which was dried over magnesium sulfate and distilled, yielding 7.75 g. of a mixture, b.p. 45–75° (6 mm.), n^{25}D 1.4920–1.5013. A solution of this mixture in an equal volume of pentane was washed with one 10-ml. and fifteen 5-ml. portions of 35% silver nitrate and five 2.5-ml. portions of 50% silver nitrate. The solution was then washed with water, dried over magnesium sulfate, and fractionated through a semi-micro column three times. The yield of very slightly yellow *n*-butylcycloöctatriene was 1.95 g. (3%), b.p. 83–85° (10 mm.), n^{25}D 1.4935–1.4987. An analytical sample had b.p. 83–85° (10 mm.), n^{25}D 1.4955, d^{25}_{4} 0.8829.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.94; H, 11.17.

Hydrogenation of a solution of 0.57 g. of III in 15 ml. of acetic acid in the presence of 0.46 g. of prereduced platinum oxide was complete in 30 minutes and required 93.8% of three molar equivalents of hydrogen. The reduction product was isolated by separating the catalyst, neutralizing the filtrate with sodium hydroxide, with cooling, and extracting with three 5-ml. portions of ether. After drying and distilling the extracts, 0.38 g. of *n*-butylcycloöctane was obtained, b.p. 89° (10 mm.), n^{25}D 1.4590, which had an infrared spectrum that was identical within experimental error with an authentic sample described below.

Cycloöctatrienes (Va and Vb) were isolated from the low boiling hydrocarbon fraction obtained from extract (3) (described above, 11.5 g.), which was dissolved in 50 ml. of pentane and extracted with five 10-ml. portions of 20% silver nitrate to remove the yellow cycloöctatetraene present (plus some of the cycloöctatrienes). The colorless pentane solution was dried over magnesium sulfate and distilled and yielded 4.9 g. (11.5%) of a mixture of cycloöctatrienes, b.p. 64–70° (80 mm.), n^{25}D 1.5052–1.5165. A maleic anhydride adduct prepared from one of the fractions with n^{25}D 1.5130 melted at 143.2–144.4° and did not depress the

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[4] A. C. Cope and F. A. Hochstein, This Journal, **72**, 2515 (1950).

[5] H. Gilman and F. W. Moore, *ibid.*, **62**, 1843 (1940).

[6] H. Gilman, F. W. Moore and O. Baine, *ibid.*, **63**, 2479 (1941).

[7] Melting points are corrected and boiling points are uncorrected. 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. The preparations and reactions of organolithium compounds were conducted under dry nitrogen.

[8] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, This Journal, **71**, 1499 (1949).

[9] A. C. Cope and L. L. Estes, Jr., *ibid.*, **72**, 1129 (1950).

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

melting point of an authentic sample of the 1,3,5-cyclooctatriene–maleic anhydride adduct.[11]

A 1.09-g. sample of the mixture of cycloöctatrienes, $n^{25}\mathrm{D}$ 1.5140, was isomerized by heating under reflux for 2 hours with 10 ml. of dry *t*-butyl alcohol containing the potassium *t*-butoxide prepared from 25 mg. of potassium.[4] The mixture was poured into 30 ml. of cold water, the hydrocarbon was separated by centrifuging, and passed through a micro column containing silica gel four times. In this manner 0.39 g. of 1,3,5-cycloöctatriene was isolated, $n^{25}\mathrm{D}$ 1.5205, $\lambda_{\max.}$ 265 mμ, $\epsilon_{\max.}$ 3480 (compare $\lambda_{\max.}$ 265 mμ, $\epsilon_{\max.}$ 3600 for pure 1,3,5-cycloöctatriene[4]). The 1,3,5-cycloöctatriene also was converted into the crystalline silver nitrate complex,[4] m.p. 125–126°.

***n*-Butylcycloöctene (VI)**.—A solution of 5.05 g. of cyclooctanone in 30 ml. of dry ether was added slowly to the *n*-butylmagnesium bromide prepared from 6.2 g. of *n*-butyl bromide and 1.0 g. of magnesium in 50 ml. of dry ether, with stirring at the reflux temperature. The mixture was heated under reflux for 3.5 hours, cooled, treated with cold saturated ammonium chloride solution, and extracted with six small portions of ether. The extracts were dried over sodium sulfate, concentrated, and a solution of the residual oil in 20 ml. of toluene was treated with a few milligrams of iodine and heated under reflux (with separation of the water formed in a Dean and Stark separator) for 5 hours. Distillation of the toluene solution through a semi-micro column yielded 3.0 g. of a light brown crude product, b.p. 68–92° (8 mm.), which was dissolved in pentane and washed with 1% sodium thiosulfate to remove iodine. The pentane solution was concentrated and the residual oil was treated with Girard reagent P to remove the cycloöctanone present. Fractional distillation of the hydrocarbon yielded 0.86 g. of *n*-butylcycloöctene (VI), b.p. 81–82° (7.8 mm.), $n^{25}\mathrm{D}$ 1.4697–1.4719. The position of the double bond was not proved, and the product may be a mixture rather than a single isomer as formulated for VI. A sample with $n^{25}\mathrm{D}$ 1.4719 was analyzed.

Anal. Calcd. for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.84; H, 13.59.

***n*-Butylcycloöctane (VII)**.—Hydrogenation of a solution of 0.63 g. of *n*-butylcycloöctene ($n^{25}\mathrm{D}$ 1.4697–1.4719) in 50 ml. of acetic acid in the presence of 0.5 g. of prereduced Adams platinum oxide catalyst was complete in 6 hours and required 106% of one molar equivalent of hydrogen. The catalyst was separated, the acetic acid was neutralized with sodium hydroxide with cooling, and the product was extracted with five 10-ml. portions of pentane. The extracts were dried over magnesium sulfate and fractionated, and yielded 0.35 g. of *n*-butylcycloöctane, b.p. 90–91° (10 mm.), $n^{25}\mathrm{D}$ 1.4585, $d^{25}{}_4$ 0.8261.

Anal. Calcd. for $C_{12}H_{24}$: C, 85.64; H, 14.36. Found: C, 85.66; H, 14.48.

Reaction of Cycloöctatetraene with Ethyllithium in Ether.—A solution of ethyllithium in 210 ml. of dry ether was prepared[8] and determined to contain 0.312 mole of the reagent by the double titration procedure of Gilman and Haubein.[12] A solution of 65 g. (0.624 mole) of cyclooctatetraene in 50 ml. of dry ether was added with stirring during 20 minutes; the temperature of the mixture rose to 29°. After heating under reflux in a bath at 55–60° for 5 hours the mixture was cooled, cold water was added slowly, and the ether layer was separated and combined with four 50-ml. ether extracts of the aqueous layer. The ether solution was washed three times with cold water, dried over magnesium sulfate, and fractionated to separate (1) 37.5 g. of a mixture of cycloöctatetraene and cycloöctatrienes, b.p. 69–72.5° (84 mm.), $n^{25}\mathrm{D}$ 1.5228–1.5239 from (2) 20.7 g. of a mixture of ethylcycloöctatetraene and ethylcyclooctatrienes, b.p. 60–72° (20 mm.), $n^{25}\mathrm{D}$ 1.5098–1.5195. Fraction (1) was diluted with an equal volume of pentane and extracted with ten 35-ml. portions of 20% silver nitrate to remove cycloöctatetraene, which left a colorless pentane solution of the cycloöctatrienes. The solution was washed with water, dried over sodium sulfate, and distilled, and yielded 10.5 g. (31%) of cycloöctatrienes, b.p. 70–73° (85 mm.), $n^{25}\mathrm{D}$ 1.5052–1.5132. A sample of the mixed cycloöctatrienes was identified by the procedure described above by isomerization with potassium *t*-butoxide to 1,3,5-cycloöctatriene, $\lambda_{\max.}$ 265 mμ, $\epsilon_{\max.}$ 3550; m.p. of the silver nitrate complex[4] 125–126°.

Ethylcycloöctatetraene (II) was separated from the high boiling fraction (2) above by extraction with two 25-ml. portions of 20% silver nitrate, after dilution with an equal volume of pentane. The yellow silver nitrate extracts were treated with an excess of concentrated ammonium hydroxide, and the yellow liquid which separated was combined with five 25-ml. pentane extracts of the aqueous layer. The pentane solution was dried over magnesium sulfate and distilled, and yielded 12.0 g. (29%) of ethylcycloöctatetraene, b. p. 81° (37 mm.), $n^{25}\mathrm{D}$ 1.5187, $d^{25}{}_4$ 0.8996.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.73; H, 9.12.

Hydrogenation of a solution of 1.633 g. of ethylcyclooctatetraene in 25 ml. of glacial acetic acid in the presence of 0.3 g. of prereduced Adams platinum oxide catalyst was complete in 1 hour and required 99% of four molar equivalents of hydrogen. The product was isolated in the same manner as VII obtained by reduction of I, and amounted to 1.2 g. of ethylcycloöctane, b.p. 83° (30 mm.), $n^{25}\mathrm{D}$ 1.4568. This sample of ethylcycloöctane was analytically pure and had an infrared spectrum that was identical with the spectrum of an authentic sample.[3]

Ethylcycloöctatriene (IV) was obtained from the colorless pentane solution from which II had been extracted with silver nitrate. The solution was washed with water, dried over magnesium sulfate and distilled through a semi-micro column. The yield of IV was 2.13 g. (5%), b.p. 75–80° (25 mm.), $n^{25}\mathrm{D}$ 1.5015–1.5200. A redistilled analytical sample was colorless and had b.p. 80–82° (30 mm.), $n^{25}\mathrm{D}$ 1.5020.

Anal. Calcd. for $C_{10}H_{14}$: C, 89.48; H, 10.52. Found: C, 89.25; H, 10.28.

Hydrogenation of a solution of 0.913 g. of IV in 25 ml. of acetic acid in the presence of 0.3 g. of prereduced Adams platinum oxide was complete in 33 minutes and required 88.5% of three molar equivalents of hydrogen. The reduction product amounted to 0.59 g. of ethylcycloöctane, b.p. 87–89° (30 mm.), $n^{25}\mathrm{D}$ 1.4568, which had an infrared spectrum that was identical with the spectrum of an authentic sample.[3]

Reaction of Cycloöctatetraene with *n*-Butyllithium in Pentane.—Cycloöctatetraene (57.4 g., 0.55 mole) was added rapidly to a solution of *n*-butyllithium prepared from 41.6 g. of *n*-butyl chloride and 6.25 g. of lithium wire in 660 ml. of olefin-free pentane (acidimetric titration of an aliquot showed that the solution contained 0.276 mole of *n*-butyllithium). The mixture was heated under reflux for 16 hours, cooled, and 150 ml. of cold water was added slowly. The pentane layer was separated and combined with five 40-ml. pentane extracts of the aqueous layer. The solution was washed with water, dried over magnesium sulfate, and concentrated. Fractionation of the residue separated 32.6 g. (57%) of recovered cycloöctatetraene, b.p. 65–67.5° (85 mm.) and 11.3 g. of butylcycloöctatriene, b.p. 75–80° (4 mm.), $n^{25}\mathrm{D}$ 1.4955–1.5066. Redistillation through a semimicro column yielded 8.15 g. (18%) of *n*-butylcycloöctatriene, b.p. 67–69.5° (2.5 mm.), $n^{25}\mathrm{D}$ 1.4970, $d^{25}{}_4$ 0.8830, $\lambda_{\max.}$ 267 mμ, $\epsilon_{\max.}$ 1650 (cyclohexane solution, Fig. 1).

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.70; H, 10.98.

Hydrogenation of a solution of 1.95 g. of *n*-butylcyclooctatriene in 25 ml. of acetic acid in the presence of 0.4 g. of prereduced Adams platinum oxide catalyst was complete in 3 hours and required 99% of three molar equivalents of hydrogen. The reduction product was 1.47 g. of *n*-butylcycloöctane, b.p. 73–74.5° (3.6 mm.), $n^{25}\mathrm{D}$ 1.4593, which had an infrared spectrum identical with an authentic sample.

Anal. Calcd. for $C_{12}H_{24}$: C, 85.64; H, 14.36. Found: C, 85.35; H, 14.20.

***s*-Butylcycloöctatriene (IX)**.—Cycloöctatetraene (44.1 g., 0.424 mole) was added during 15 minutes to the *s*-butyllithium prepared from 41.6 g. of *s*-butyl chloride and 6.24 g. of lithium wire in 780 ml. of olefin-free pentane (0.212 mole of *s*-butyllithium was present according to acidimetric titration of an aliquot). The exothermic reaction caused refluxing during the addition, and the mixture was heated

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(11) A. C. Cope, H. R. Nace and L. L. Estes, Jr., THIS JOURNAL, **72**, 1123 (1950).

(12) H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

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.), $n^{25}\text{D}$ 1.4947, d^{25}_4 0.8879, $\lambda_{\text{max.}}$ 270 mμ, $\epsilon_{\text{max.}}$ 1740 (in cyclohexane, Fig. 1).

Anal. Calcd. for $C_{12}H_{18}$: 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.), $n^{25}\text{D}$ 1.4630, with an infrared spectrum identical with that of an authentic sample described below.

Anal. Calcd. for $C_{12}H_{24}$: C, 85.64; H, 14.36. Found: C, 85.54; H, 14.07.

1-*s*-Butylcycloöctanol.—A solution of 6.96 g. of cyclooctanone 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.), $n^{25}\text{D}$ 1.4840, d^{25}_4 0.9462.

Anal. Calcd. for $C_{12}H_{24}O$: 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.), $n^{25}\text{D}$ 1.4725–1.4755. An analytical sample had b.p. 83.5° (10 mm.), $n^{25}\text{D}$ 1.4739.

Anal. Calcd. for $C_{12}H_{22}$: 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 prereduced 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.), $n^{25}\text{D}$ 1.4629.

Anal. Calcd. for $C_{12}H_{24}$: C, 85.64; H, 14.36. Found: C, 85.68; H, 14.38.

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

Cyclic Polyolefins. XXII. Substituted Cycloöctatetraenes from Substituted Acetylenes[1]

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, phenylcyclooctatetraene 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 communication[2] that the copolymerization of substituted acetylenes with acetylene under conditions similar to those used for the polymerization of acetylene to cyclooctatetraene[3] 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 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

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[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).

[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).