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

Cyclic Polyolefins. XXIV. 1,2-Diphenylcycloöctatetraene[1]

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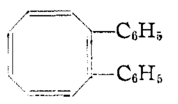
1,2-Diphenylcycloöctatetraene (I) has been prepared by copolymerization of diphenylacetylene with acetylene; *o*-diphenylbenzene was formed as a by-product. Evidence for the structure of 1,2-diphenylcycloöctatetraene was obtained by hydrogenation, in which a large amount of *cis*- and a small amount of *trans*-1,2-diphenylcycloöctane were formed. The structure of *cis*-1,2-diphenylcycloöctane was confirmed by an independent synthesis from 2-phenylcycloöctanone. 2,3-Diphenyl-1,3-cycloöctadiene and 1,2-diphenylcycloöctene were isolated from partial hydrogenations of I. Evidence for their structures was obtained from ultraviolet absorption spectra and quantitative hydrogenations.

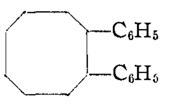
The method of synthesis of substituted cycloöctatetraenes by copolymerization of substituted acetylenes with acetylene described recently[2] now has been extended to the preparation of 1,2-diphenylcycloöctatetraene (I) from diphenylacetylene. In addition to I (14%), *o*-diphenylbenzene (11%) and recovered diphenylacetylene (6%) were isolated from the reaction mixture after steam distillation to remove volatile products (principally benzene and cycloöctatetraene) by extraction with benzene, and separated by a combination of distillation and crystallization.

1,2-Diphenylcycloöctatetraene (I) (or the isomer with a single bond between the carbon atoms to which the phenyl groups are attached) was isolated as a pale yellow-green crystalline solid, m.p. 112.4–112.8°, that was characterized by ultraviolet and infrared spectra (Figs. 1 and 3), and by quantitative hydrogenation with the absorption of 99% of four molar equivalents of hydrogen. Crystallization of the reduction product yielded 1,2-diphenylcycloöctane (believed to be the *cis* isomer, IIa) m.p. 75.8–76.5°, which has been synthesized by an independent route described below. A small amount of an isomer, believed to be *trans*-1,2-diphenylcycloöctane (IIb), m.p. 34.4–35° was isolated from the mother liquors by chromatography on alumina followed by fractional crystallization.

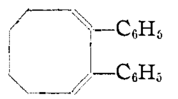
Partial reduction of I with the absorption of 96% of three molar equivalents of hydrogen formed a mixture from which 2,3-diphenyl-1,3-cycloöctadiene (III), m.p. 113.3–113.7°, was isolated by fractional crystallization. The structure assigned to III is based on quantitative reduction with the absorption of 98% of two molar equivalents of hydrogen forming 1,2-diphenylcycloöctane (IIa), and on the ultraviolet absorption spectrum. The ultraviolet spectrum of III, with an absorption maximum at 247 mμ (ε 25,900), is similar to the spectrum of 2,3-diphenyl-1,3-butadiene, which has a maximum at 243 mμ (ε 18,100) (Fig. 2). Another partial reduction of I in which 114% of three molar equivalents of hydrogen were absorbed formed a mixture from which small amounts of III and 1,2-diphenylcycloöctene (IV), m.p. 77.4–77.7°, were isolated by crystallization and chromatography on alumina. The ultraviolet absorption spectrum of IV (Fig. 2) contains a maximum at 254 mμ (ε 8,110) and an inflection at 223 mμ (ε 11,300) indicating the presence of a second maximum near this wave length. Only structure IV and the other isomer in which the double bond is conjugated with a phenyl group (2,3-diphenylcycloöctene) would be expected to absorb so strongly in the ultraviolet. The spectrum of the latter compound should be similar to the spectrum of 2,3-diphenylcyclohexene, which has a single maximum at 246 mμ (ε 11,680).[3] On the basis of the difference between the spectrum of 2,3-diphenylcyclohexene and the observed spectrum, structure IV can be assigned to the product with considerable certainty. Quantitative reduction of IV resulted in the absorption of 97% of one molar equivalent of hydrogen in ethyl acetate solution in the presence of palladium-on-carbon and appeared to form only the isomer of 1,2-diphenylcycloöctane melting at 75.8–76.5°. By analogy with other cases in which hydrogenation has resulted in *cis* addition,[4] this isomer is believed to be *cis*-1,2-diphenylcycloöctane (IIa).



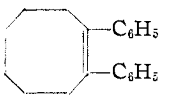
I



cis, IIa, m.p. 75.8–76.5°
trans, IIb, m.p. 34.4–35°



III



IV

An independent synthesis of 1,2-diphenylcycloöctane was undertaken to confirm the structure of I. 1-Phenylcycloöctene[5] was converted to the epoxide by treatment with peracetic acid, and the epoxide was heated with acetic acid containing a small amount of sulfuric acid, forming a mixture of the isomeric hydroxy acetates (VI). The tertiary hydroxyl or acetate group appeared to be eliminated during the reaction or on distillation, for the product was a crude mixture of 2-phenyl-2-cycloöcten-1-ol (VIIa) and 2-phenyl-2-cycloöcten-1-yl acetate (VIIb). Saponification of the mixture yielded the alcohol VIIa, which was converted into 2-phenylcycloöctanol by hydrogenation, and subsequently into 2-phenylcycloöctanone (VIII, 47% from 1-phenylcycloöctene) by oxidation with chromic acid in acetic acid. The ketone VIII obtained

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(1) Supported in part by the Office of Naval Research under Contract N5ori-07822, Project Designation NR-055-96.

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

(3) G. P. Mueller, J. G. Fleckenstein and W. H. Tallent, *ibid.*, **73**, 2651 (1951).

(4) E. Ott, A. Behr and R. Schröter, *Ber.*, **61B**, 2124 (1928); F. v. Wessely and H. Welleba, *ibid.*, **74B**, 777 (1941); H. A. Weidlich and M. Meyer-Delius, *ibid.*, **74B**, 1195 (1941).

(5) A. C. Cope and A. A. D'Addieco, THIS JOURNAL, **73**, 3419 (1951).

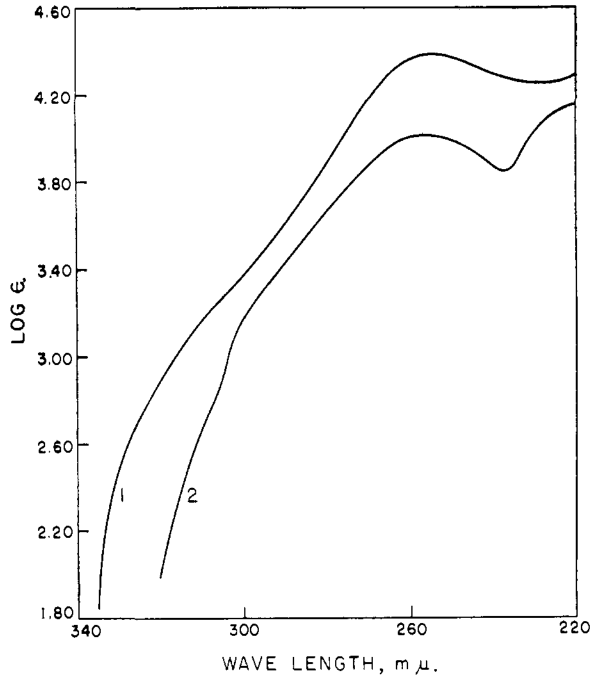


Fig. 1.—Ultraviolet absorption spectra in cyclohexane: curve 1, 1,2-diphenylcycloöctatetraene (I); curve 2, 2-phenyl-1,3-cycloöctadiene (X).

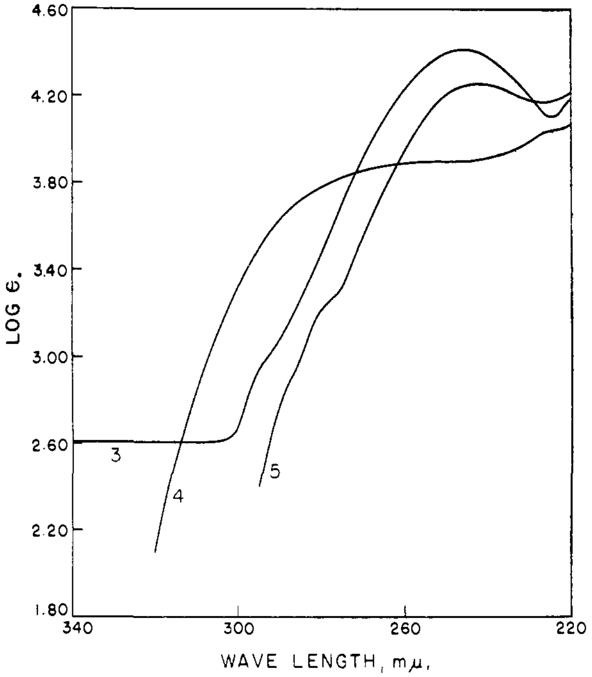


Fig. 2.—Ultraviolet adsorption spectra in cyclohexane: curve 3, 2,3-diphenyl-1,3-cycloöctadiene (III); curve 4, 1,2-diphenylcycloöctene (IV); curve 5, 2,3-diphenyl-1,3-butadiene.

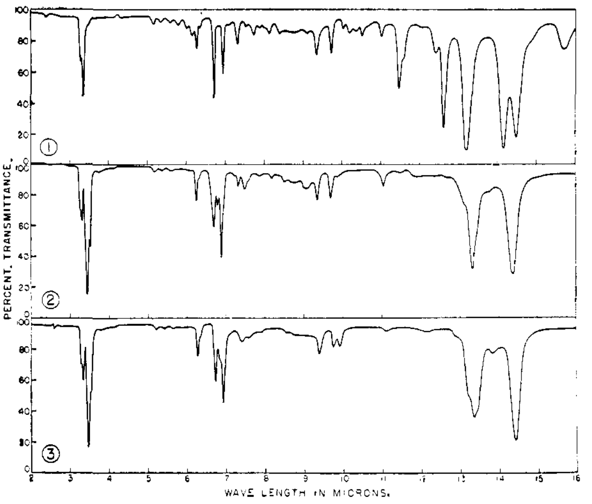
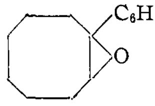
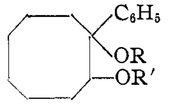


Fig. 3.—Infrared absorption spectra of solutions (100 mg./ml.) in carbon tetrachloride in the region 2–12μ and in carbon disulfide in the region 12–16μ: curve 1, 1,2-diphenylcycloöctatetraene (I); curve 2, *cis*-1,2-diphenylcyclooctane (IIa); curve 3, *trans*-1,2-diphenylcycloöctane (IIb).

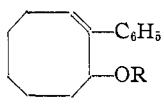
by this sequence was characterized by analysis, preparation of a crystalline semicarbazone, and reduction by a modified Wolff–Kishner method[6] to phenylcycloöctane, which was identical with an authentic sample (mixed melting point). Addition of phenyllithium to VIII formed 1,2-diphenylcycloöctanol (IX), m.p. 73.5–74.5°, from which 1,2-diphenylcycloöctene was prepared by dehydration with iodine in refluxing toluene. This olefin was not obtained in sufficient quantity to permit separation of isomers, but quantitative hydrogenation resulted in the absorption of 98% of one molar equivalent of hydrogen, and the pure isomer of 1,2-diphenylcycloöctane melting at 75.8–76.5° (IIa) was isolated from the product by crystallization. It was proved to be identical with IIa prepared by hydrogenation of I by mixing melting point and comparison of the infrared spectra.



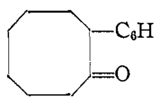
V



VIa, R = Ac, R' = H
VIb, R = H, R' = Ac



VIIa, R = H
VIIb, R = Ac



VIII

Incidental to the synthesis described above, 2-phenyl-1,3-cycloöctadiene (X) was prepared (in 40% yield from 1-phenylcycloöctene) by heating the mixture of alcohol and acetate (VIIa and VIIb) with zinc chloride. The liquid diene X was characterized by quantitative reduction to phenylcycloöctane with the absorption of 100% of two molar equivalents of hydrogen, and by the ultraviolet spectrum (Fig. 1). The absorption maximum at 256 mμ (ε 10,600) in the spectrum indicates that the phenyl group and both double bonds are in conjugation. Only structure X and 1-phenyl-1,3-cycloöctadiene have such conjugated systems, and the latter compound has been prepared previously[7] and has different properties (λ_{max} 265 mμ, ε 12,300).

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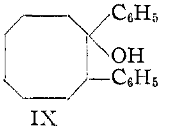
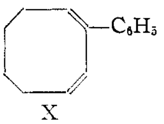
(6) Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

(7) A. C. Cope and E. C. Hermann, *ibid.*, **72**, 3405 (1950); D. F. Rugen, Ph.D. Thesis, Massachusetts Institute of Technology, June, 1952.

The ozonization of X yielded benzoic acid and adipic acid as expected, but the yield of adipic acid (1%) was too small to serve as conclusive structural evidence.



IX



X

Experimental[8]

1,2-Diphenylcycloöctatetraene (I).—Diphenylacetylene[9] (40 g.) was copolymerized with acetylene in tetrahydrofuran as a solvent in the presence of nickel acetylacetonate catalyst and calcium carbide by the general procedure described previously.[2] Acetylene absorption amounted to 975 p.s.i. in a period of 9.5 hours at 80–90°. The reaction mixture was steam distilled until organic material was distilling very slowly and was blue-green in color. The water was decanted from the tarry residue, which was placed in a large soxhlet thimble and extracted with benzene for 4 days, until the extracts were nearly colorless. A small amount of hydroquinone was added as a polymerization inhibitor during the extraction, and the extracts were replaced by an equal volume of benzene every 24 hours to avoid longer heating of the products in the extracts. Distillation of the organic layer from the steam distillate yielded benzene, 40 g. of cycloöctatetraene, and small amounts of higher boiling byproducts from the polymerization of acetylene. The benzene extracts from the non-volatile tarry residue were concentrated and distilled in a short path still at 0.2 mm. The crude distillate was boiled with pentane and filtered to remove insoluble hydroquinone. A yellow-green solid separated from the filtrate on concentrating and cooling. The solid was separated, and the dark blue-green solution was extracted with 85% phosphoric acid (to remove azulene) until it was light yellow-green in color, washed with water, and concentrated. The residue was distilled through a semi-micro column.[10] A fraction boiling at 65–111° (0.13 mm.) was recrystallized from 95% ethanol and yielded 2.5 g. (6%) of recovered diphenylacetylene, m.p. 61.6–63.8°, identified by mixed melting point with a known sample. The second fraction, b.p. 111–120° (0.12 mm.), was crystallized from 95% ethanol and yielded 5.7 g. (11%) of *o*-diphenylbenzene, m.p. 55.8–57.4°. Two additional crystallizations from absolute ethanol gave a pure sample, m.p. 58–58.7°, which was identified by analysis and comparison with an authentic sample (mixed melting point and infrared spectrum).

A short path distillation at 210° and 0.3 mm. of the residue from the distillation described above yielded more of the yellow-green solid obtained before from the pentane solution, and these solids were combined and treated with Darco in boiling absolute ethanol. On filtration and cooling 7.9 g. (14%) of 1,2-diphenylcycloöctatetraene (I) was obtained as pale yellow-green crystals, m.p. 112.4–112.8°.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29; mol. wt., 256. Found: C, 93.71; H, 6.52; mol. wt., 280 (Rast method in camphor).

Hydrogenation of a solution of 0.58 g. of I in 8 ml. of ethyl acetate in the presence of 0.3 g. of 10% palladium-on-Norit was complete in 6 hours and 99% of four molar equivalents of hydrogen was absorbed. Three crystallizations of the product from absolute ethanol yielded pure *cis*-1,2-diphenylcycloöctane (IIa), m.p. 75.8–76.5°, which did not depress the melting point of an authentic sample described below. The infrared spectrum of this sample (Fig. 3) was identical with the spectrum of the authentic sample.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.90; H, 9.10.

2,3-Diphenyl-1,3-cycloöctadiene (III).—Hydrogenation of a solution of 1.12 g. of I in 25 ml. of ethyl acetate in the presence of 0.2 g. of 1% palladium-on-calcium carbonate[11] proceeded extremely slowly, and three separate additions of 0.5-g. portions of the catalyst did not markedly increase the rate. After 9 hours and the absorption of 77% of three molar equivalents of hydrogen, 0.1 g. of 10% palladium-on-Norit was added, followed by 0.2 g. 1 hour later. The reduction was stopped after a total of 16 hours, at which time 96% of three molar equivalents of hydrogen had been absorbed. The catalyst was separated and the filtrate was concentrated, yielding an oil that was crystallized from absolute ethanol. A white solid was obtained in a yield of 0.35 g., m.p. 96–105°. Three recrystallizations from absolute ethanol yielded 0.19 g. of pure 2,3-diphenyl-1,3-cycloöctadiene (III), m.p. 113.3–113.7°.

Anal. Calcd. for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.21; H, 7.92.

Hydrogenation of a solution of 0.12 g. of III in 5 ml. of methanol in the presence of 0.2 g. of 10% palladium-on-Norit was complete in 30 minutes, and 98% of two molar equivalents of hydrogen was absorbed. The product was isolated in a yield of 0.089 g., m.p. 61–65°. Three crystallizations from absolute ethanol yielded pure *cis*-1,2-diphenylcycloöctane (IIa), m.p. 73.6–74.4°, proved by mixed melting point to be identical with a sample obtained from I by reduction in one step.

1,2-Diphenylcycloöctene (IV).—A solution of 3.0 g. of I in 25 ml. of ethyl acetate was hydrogenated in the presence of 0.4 g. of 10% palladium-on-Norit, and an additional 0.3-g. portion of the catalyst was added after 5.5 hours. The reduction was stopped after 22.5 hours, when 114% of three molar equivalents of hydrogen had been absorbed. The product was isolated in the same manner as III, except that methanol was used as the solvent. A total of 2.5 g. of a white solid obtained as three crops, each melting over a wide range, was fractionally crystallized from 1:1 absolute ethanol–methanol. The least soluble fraction (0.40 g., m.p. 44–70°) was chromatographed on a 15 × 1.2-cm. column containing 16 g. of Merck reagent alumina, and eluted with pentane. Evaporation of the effluent (50 ml.) and three crystallizations of the residue from absolute ethanol yielded 0.16 g. of 1,2-diphenylcycloöctene (IV), m.p. 77.4–77.7°; mixed m.p. with IIa, 47–57°.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.58; H, 8.46.

Hydrogenation of a solution of 0.10 g. of IV in 5 ml. of ethyl acetate in the presence of 0.3 g. of 10% palladium-on-Norit was complete in 20 minutes, and 97% of one molar equivalent of hydrogen was absorbed. The product obtained after filtration to separate the catalyst and evaporation of the solvent was practically pure *cis*-1,2-diphenylcycloöctane (IIa), m.p. 72.9–74.5°. Recrystallization from absolute ethanol yielded pure IIa, m.p. and mixed m.p. with a sample obtained by reduction of I in one step, 75.3–75.6°.

***trans*-1,2-Diphenylcycloöctane (IIb).**—The mother liquors remaining from isolation of III and IV from the partial hydrogenation of I were concentrated, and a solution of the residue in 25 ml. of ethyl acetate was hydrogenated in the presence of 3.0 g. of 10% palladium-on-Norit. The reduction was stopped after 94 hours, when hydrogen absorption had become very slow. The catalyst was separated and the solvent evaporated, and the residue was crystallized from absolute ethanol, yielding 1.07 g. of fairly pure *cis*-1,2-diphenylcycloöctane (IIa), m.p. 72.2–74.1°. Two more crops of less pure IIa were obtained by concentrating the mother liquor (1.01 g., m.p. 65–70.6°). The viscous liquid residue remaining after removing all of the solvent (1.12 g.) was dissolved in pentane and chromatographed on an 83 × 3-cm. column containing 70 g. of activated alumina. The column was eluted with 200 ml. of pentane, and the effluent was collected in 10-ml. fractions. Most of the *cis* isomer IIa was collected in the first ten fractions. The remaining fractions were concentrated and the residue was recrystallized from absolute ethanol. Several small crops of impure IIa separated first, after which the low melting *trans*-1,2-diphenylcycloöctane (IIb) crystallized from the mother liquors. Two recrystallizations from absolute ethanol yielded 0.081 g. of IIb, m.p. 33.4–34.6°. A sample of IIb recrystallized for analysis from absolute ethanol melted at 34.4–35°.

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[8] Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses. Infrared spectra were determined with a Baird Double Beam Infrared Recording Spectrometer, Model B, fitted with a sodium chloride prism. Ultraviolet spectra were determined with a Cary Ultraviolet Recording Spectrophotometer, Model 11 MS.

[9] W. Schlenk, E. Bergmann and I. Rodloff, *Ann.*, **463**, 76 (1928).

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

[11] M. Busch and H. Stöve, *Ber.*, **49**, 1063 (1916).

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.66; H, 9.18.

2-Phenylcycloöctanone (VIII).—Anhydrous sodium acetate (1.5 g.) was added to 8.7 g. of commercial 40% peracetic acid (Becco Sales Corp.) to neutralize the sulfuric acid present, and the solution was added slowly with stirring to 4.21 g. of 1-phenylcycloöctene, with intermittent cooling to keep the temperature at 20–30°. The solution was stirred for one hour longer at room temperature, and poured onto 40 g. of ice. The mixture was neutralized with cold aqueous sodium hydroxide and extracted with ether. The extracts were washed and distilled through a semi-micro column, and yielded 4.42 g. of crude 1-phenylcycloöctene oxide (V), b.p. 99–100° (0.24 mm.). This compound was heated at 65° for 1 hour with 15 ml. of glacial acetic acid containing 1 drop of concentrated sulfuric acid. The product was isolated in the same manner as V, and amounted to 4.46 g. of a crude mixture containing 2-phenyl-2-cycloöcten-1-ol (VIIa) and 2-phenyl-2-cycloöcten-1-yl acetate (VIIb), b.p. 101–116° (0.23 mm.). This mixture was heated under reflux with 1.26 g. of potassium hydroxide in 20 ml. of 95% ethanol for 1 hour. The solution was poured into 300 ml. of water and the product was extracted with ether. The extracts were washed, concentrated, and the residue was distilled through a semi-micro column, yielding 3.29 g. of crude 2-phenyl-2-cycloöcten-1-ol (VIIa), b.p. 106–128° (0.4–1.0 mm.). A solution of this material in 15 ml. of absolute ethanol was hydrogenated in the presence of 0.5 g. of 10% palladium-on-Norit during a period of 12 hours. After separation of the catalyst and concentration of the filtrate, distillation of the residue yielded 3.20 g. of crude 2-phenylcycloöctanol, b.p. 85–113° (0.37 mm.). A solution of the 2-phenylcyclooctanol in 10 ml. of glacial acetic acid was cooled and oxidized by addition of a solution of 1.1 g. of chromic anhydride in 5 ml. of water and 12.5 ml. of acetic acid with stirring at 0–5° over a period of 1.5 hours. After an additional 0.5 hour the solution was allowed to come to room temperature and stirred for 2 hours. The mixture was cooled, neutralized with sodium hydroxide, and extracted with ether. The extracts were washed with water, concentrated, and the residue was distilled through a semi-micro column, yielding 2.20 g. (47% over-all from 1-phenylcycloöctene) of 2-phenylcyclooctanone (VIII), b.p. 110–112° (0.31 mm.), $n^{25}D$ 1.5412–1.5418. The mid-fractions (1.34 g.) had $n^{25}D$ 1.5417.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.00; H, 8.91.

2-Phenylcycloöctanone semicarbazone was prepared by adding 70 mg. of semicarbazide hydrochloride and 55 mg. of sodium acetate to a hot solution of 94 mg. of VIII in 2 ml. of 50% aqueous ethanol. The semicarbazone crystallized on cooling; 73 mg., m.p. 152.3–154.5° (dec.). Recrystallization from 70% ethanol yielded an analytical sample, m.p. 153.9–154.7° (dec., introduced at 148°).

Anal. Calcd. for $C_{15}H_{21}N_3O$: C, 69.46; H, 8.16; N, 16.21. Found: C, 69.28; H, 8.25; N, 16.37.

2-Phenylcycloöctanone was reduced by the Wolff–Kishner method by heating 0.15 g. of VIII with 1.0 ml. of 85% hydrazine hydrate and 0.5 g. of potassium hydroxide in 10 ml. of ethylene glycol from 185 to 220° in 1 hour, and at 220° for 3 hours. The solution was cooled, added to 50 ml. of water, and the product was extracted with ether. The extracts were washed with water, concentrated, and the residue was distilled, yielding 0.041 g. (29%) of phenylcyclooctane, $n^{25}D$ 1.5350, m.p. −3.0 to 2.1°, and mixed m.p. with an authentic sample (m.p. 7.1–7.8°), −1.1 to 4.5°.

1,2-Diphenylcycloöctanol (IX).—A solution of 2.06 g. of VIII in 5 ml. of ether was added to the phenyllithium prepared from 0.28 g. of lithium wire and 3.14 g. of bromobenzene in 15 ml. of dry ether. The mixture was heated under reflux for 1 hour, water was added, and the ether layer was separated. The ether was distilled, and a solution of the residue and a small crystal of iodine in 50 ml. of benzene was heated under reflux for 3 hours. The solution was cooled, washed with sodium thiosulfate solution, and concentrated. The residue was distilled in a short path still at 0.4 mm. with a heating block temperature of 170°. The distillate was heated under reflux for 2 hours with a solution of 1.0 g. of Girard reagent "T" in 9 ml. of ethanol and 1 g. of acetic acid to remove any of the ketone VIII that might be present. The product was isolated by adding the mixture to water, neutralizing it with sodium carbonate, extracting with ether, and repeating the short path distillation. The distillate was a mixture of 1,2-diphenylcycloöctanol (IX) and diphenylcycloöctene, from which crystals of IX separated. They were purified by sublimation and two crystallizations from 95% ethanol; the yield of pure IX was 0.086 g., m.p. 73.5–74.5°.

Anal. Calcd. for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.44; H, 8.71.

***cis*-1,2-Diphenylcycloöctane (IIa).**—The viscous liquid distillate from which IX had been isolated (0.65 g.) was heated with a crystal iodine in refluxing toluene for 22 hours to complete conversion of the alcohol to olefin. The product was washed with sodium thiosulfate, purified by a short path distillation, dissolved in pentane and passed through a micro column of silica gel to remove any of the alcohol IX that was present. After this treatment and decolorization with Darco the olefin was slightly impure according to analysis (Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 90.90; H, 8.50). A 0.34-g. sample was dissolved in 5 ml. of ethyl acetate and 5 ml. of methanol, and hydrogenated in the presence of 0.2 g. of 10% palladium-on-Norit. Another 0.3-g. portion of the catalyst was added after 1 hour. Hydrogen absorption stopped after 3 hours, and amounted to 98% of one molar equivalent. After separation of the catalyst and evaporation of the filtrate, four crystallizations of the residue from 95% ethanol yielded 0.124 g. of pure *cis*-1,2-diphenylcycloöctane, m.p. 75.6–76.2°.

2-Phenyl-1,3-cycloöctadiene (X).—Oxidation of one 4.24-g. sample of 1-phenylcycloöctene with peracetic acid by the procedure described above yielded 4.14 g. of a mixture of 2-phenyl-2-cycloöcten-1-ol and 2-phenyl-2-cycloöcten-1-yl acetate (VIIa and VIIIb) rather than the epoxide V as expected, probably because acetic acid was present in the crude product during distillation. One portion of this product was heated with 50 mg. of zinc chloride at 165–170° for 2 hours, and the remainder was distilled from approximately 50 mg. of zinc chloride at 93–95° (0.2 mm.). Both procedures yielded the crude diene X, and the products (2.44 g.) were combined and treated with Girard reagent "T" according to the procedure described above to remove any ketone that might have been formed by molecular rearrangement. Distillation of the product through a semi-micro column yielded 1.66 g. (40%) of 2-phenyl-1,3-cycloöctadiene (X), b.p. 90–91° (0.27 mm.), $n^{25}D$ 1.5806–1.5828. A solution of 0.9 g. of this product was passed through a semi-micro column of silica gel to remove any oxygen-containing impurities and redistilled, yielding 0.48 g. of pure X, b.p. 88–90° (0.24 mm.), $n^{25}D$ 1.5812, d^{25}_4 1.028.

Anal. Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.18; H, 8.82.

Hydrogenation of a solution of 0.23 g. of X in 5 ml. of methanol in the presence of 0.2 g. of 10% palladium-on-Norit was complete in 2.3 hours and 100% of two molar equivalents of hydrogen was absorbed. Distillation of the product yielded 0.18 g. of phenylcycloöctane, $n^{25}D$ 1.5300, m.p. 4.4–7.0° and mixed m.p. with an authentic sample, 5.6–7.4°.

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