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

Cyclic Polyolefins. XXIII. Valence Tautomerism of 1,3,5-Cycloöctatriene and Bicyclo[4.2.0]octa-2,4-diene[1]

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1,3,5-Cycloöctatriene (I) has been found to be in mobile equilibrium with a bridged isomer, bicyclo[4.2.0]octa-2,4-diene (II). Both I and II have been isolated as pure hydrocarbons, and equilibrated to the same mixture (85% I and 15% II) by heating briefly at 80–100°. The structure of II has been established by reduction to bicyclo[4.2.0]octane, oxidation to *cis*-1,2-cyclobutanedicarboxylic acid, and study of Diels–Alder adducts formed with maleic anhydride and dimethyl acetylenedicarboxylate. Pyrolysis of the latter formed cyclobutene and dimethyl phthalate in a reaction that provides an advantageous synthetic route to cyclobutene. The dynamic isomerism of I and II is a case of "valence tautomerism," in which no atoms or groups shift. The only changes that occur are electronic displacements required to interchange double and single bonds and open or close the bridged ring of II, with corresponding changes in interatomic distances and angles.

The preparation of 1,3,5-cycloöctatriene (I) from cycloöctatetraene and its purification through a crystalline silver nitrate complex were reported recently.[3] The pure triene I, regenerated from the silver nitrate complex, was reducible to pure cyclooctane. When heated, I was isomerized to a mixture of hydrocarbons which on reduction yielded cycloöctane containing 5–10% of bicyclo[4.2.0]-octane. This paper reports the isolation and identification of bicyclo[4.2.0]octa-2,4-diene (II), the compound formed by thermal isomerization of I, and presents evidence that I and II comprise a system in dynamic equilibrium.

The synthesis of I has been improved by reduction of cycloöctatetraene with sodium in a mixture of liquid ammonia and ether. The product, a mixture of I, bicyclo[4.2.0]octa-2,4-diene (II) (see below), 1,3,6-cycloöctatriene and cycloöctatetraene, was washed with aqueous silver nitrate to remove cycloöctatetraene, and then heated with potassium *t*-butoxide in *t*-butyl alcohol to convert the 1,3,6-triene into the conjugated isomer. The resulting mixture of I and II was treated with silver nitrate and yielded the crystalline complex, I·AgNO$_3$, m.p. 125–126°, from which pure I, n^{25}D 1.5249, was regenerated with ammonium hydroxide. While I could be distilled unchanged at temperatures below 40°, slow distillation at about 85° (120 mm.) yielded a mixture of I and an isomeric hydrocarbon with a lower boiling point and lower refractive index. The isomer was isolated by removing I from the mixture as the crystalline silver nitrate complex, and purified by washing with 50% aqueous silver nitrate, in which it was less soluble than was I. The pure isomer (n^{25}D 1.5035) obtained in this way could be distilled unchanged below 30°. Evidence that it was bicyclo[4.2.0]octa-2,4-diene (II) was obtained by quantitative hydrogenations, in which 100–102% of two molar equivalents of hydrogen was absorbed and bicyclo-[4.2.0]octane was formed. The hydrocarbons I and II were characterized by ultraviolet (Fig. 1) and infrared absorption spectra (Fig. 2). The ultraviolet spectra were very similar, with the absorption maximum of the bridged diene II occurring at a slightly longer wave length than the maximum of the triene I. A similar relationship between the ultraviolet absorption maxima of cycloöctatetraene dichloride and dibromide (dihalides with the bridged bicyclo[4.2.0]octa-2,4-diene nucleus) and 1,3,5-cycloöctatriene has been observed previously.[4]

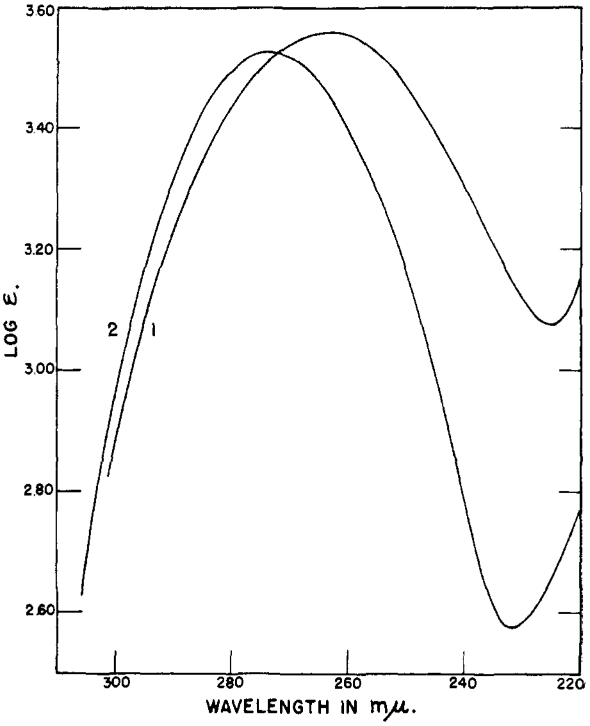
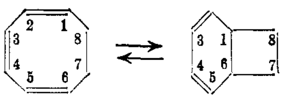


Fig. 1.—Ultraviolet absorption spectra of cyclohexane solutions, determined with a Beckman model DU quartz ultraviolet spectrophotometer: curve 1, 1,3,5-cycloöctatriene (I), $\lambda_{max.}$ 265 mμ (ϵ 3600) and $\lambda_{min.}$ 225 mμ (ϵ 1190) (ref. 3); curve 2, bicyclo[4.2.0]octa-2,4-diene (II), $\lambda_{max.}$ 274 mμ (ϵ 3340), $\lambda_{min.}$ 232 mμ (ϵ 374).



I II

Evidence confirming the structures assigned to I and II was obtained by oxidation of the hydrocarbons. Ozonization of I, followed by treatment of the ozonide with hydrogen peroxide, yielded succinic acid. The bridged diene II gave mixtures containing polymeric products on ozonization, but

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[1] Presented at the Buffalo Meeting of the American Chemical Society, Division of Organic Chemistry, March 24, 1952.

[2] du Pont Postdoctorate Fellow.

[3] A. C. Cope and F. A. Hochstein, THIS JOURNAL, **72**, 2515 (1950).

[4] A. C. Cope and M. Burg, *ibid.*, **74**, 168 (1952).

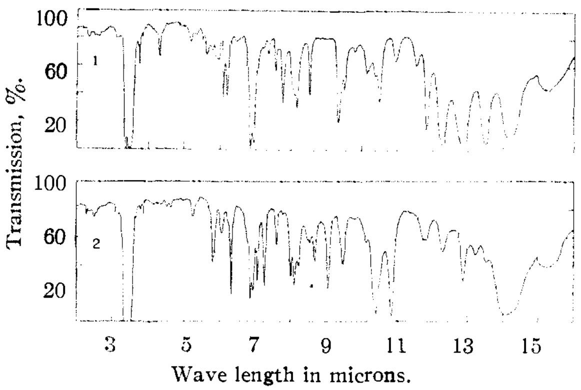


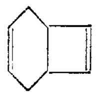
Fig. 2.—Infrared absorption spectra of pure liquids in an 0.025-mm. cell, determined with a Baird double beam infrared recording spectrometer, model B, fitted with a sodium chloride prism: curve 1,1,3,5-cycloöctatriene (I); curve 2, bicyclo[4.2.0]octa-2,4-diene (II).

oxidation with sodium permanganate in acid solution formed *cis*-1,2-cyclobutanedicarboxylic acid, which was isolated in 39% yield.

Since the results of both quantitative hydrogenation and oxidative degradation support structures I and II, the rearrangement of I to II by heating must consist in the establishment of a bridge across the eight-membered ring. An alternate explanation of the isomerization of I and II as an interconversion of geometric isomers appears to be very unlikely in view of the structural evidence, since a consequence of that interpretation would be that one of the isomers must form a bridged structure containing a four-membered ring on both hydrogenation and oxidation.

Samples of either pure I or pure II that were heated at 100° for one hour formed mixtures of I and II. These mixtures had the same refractive index ($n^{25}\text{D}$ 1.5216) and identical infrared spectra containing the absorption bands characteristic of the two hydrocarbons. In addition to the isolation of II from I after heating previously described, II was heated and the crystalline silver nitrate complex of I was isolated from the mixture of I and II that was formed. Accordingly the isomerization of I and II is reversible, and the refractive index of 1.5216 corresponds to an equilibrium value. Determination of the refractive index of known mixtures of I and II showed that the composition–refractive index curve of the two isomers is linear; accordingly the observed refractive index corresponds to a composition of 85% of I and 15% of II in the equilibrium mixture.

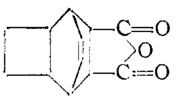
Ziegler and Wilms[5] have formulated the initial product formed by reduction of cycloöctatetraene with sodium and methylaniline in ether as bicyclo[4.2.0]octa-3,7-diene because it was not reduced further by an excess of sodium, and state that this hydrocarbon on heating rearranges into 1,3,5-cycloöctatriene. Although their conditions of reduction differ from those used in the present work, and might lead to a different product, our observation that I and II are readily equilibrated by heating suggests that their product may have contained II.



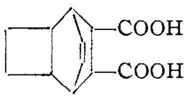
Bicyclo[4.2.0]octa-3,7-diene

The term "valency tautomerism" has been suggested for reversible isomerizations such as the interconversion of I and II, in which no atoms or groups shift.[6] Only electronic displacements corresponding to interconversion of double and single bonds occur in the isomerization, with corresponding changes in bond distances and angles. In the conversion of I to II the carbon atoms forming the six-membered ring of II become approximately coplanar, and the transannular distance between C_1 and C_6 of I is shortened to the length of a carbon–carbon single bond. The reaction is formally equivalent to an intramolecular Diels–Alder addition, in which C_1 (of I) adds to C_6, and C_4 adds to C_5 (forming a double bond).

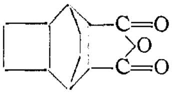
In another approach to the synthesis of I and II, cycloöctatetraene dibromide, which has a bridged ring structure,[4,7] was reduced with lithium aluminum hydride in the presence of sodium iodide. The product was a mixture of I and II, with I being formed through bridge opening.



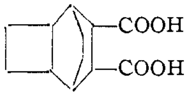
III



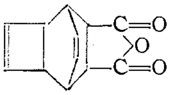
IV



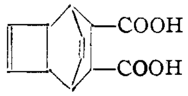
V



trans-acid, VI
cis-acid, VII



VIII



cis-acid, IX
trans-acid, X

Further evidence concerning the structure and reactivity of the bridged diene II was obtained by study of the Diels–Alder adducts formed with maleic anhydride and with dimethyl acetylenedicarboxylate. Maleic anhydride and II reacted in benzene solution at 10° to form the adduct III. The triene I failed to react with maleic anhydride under these conditions, but in benzene at 60–80° (a temperature that would equilibrate I and II) formed the same adduct, III. Saponification of the anhydride formed the corresponding *cis*-acid, IV. Hydrogenation of a solution containing esters of IV prepared by dissolving III in ethanol containing hydrochloric acid resulted in the absorption of 100% of one molar equivalent of hydrogen. Saponification of the reduction product and sublimation of the acids formed resulted in separation of the saturated *cis*-anhydride, V, which sublimed, from a residue of the saturated *trans*-acid, VI. Partial conversion of the *cis*- to *trans*-acid undoubtedly occurred during the alkaline hydrolysis. The *cis*-acid

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(5) K. Ziegler and H. Wilms, *Ann.*, **567**, 23 (1950).

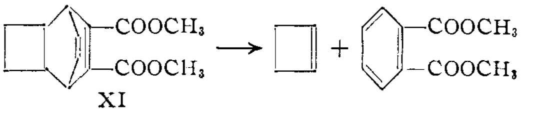
(6) J. W. Baker, "Tautomerism," George Routledge and Sons, London, 1934, pp. 201–226.

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

VII was formed by hydrolysis of the anhydride V. It was possible to relate the series of acids and anhydrides III to VII with the cycloöctatetraene–maleic anhydride adduct VIII, from which all of the compounds III to VII could be prepared by procedures similar to those described in ref. 7. A solution of the potassium salt of the *cis*-acid IX was prepared by dissolving VIII in dilute potassium hydroxide. Hydrogenation of the solution was interrupted after absorption of one molar equivalent, and acidification followed by sublimation formed the anhydride III. Accordingly the double bond in IX that is reduced on partial hydrogenation is in the four- rather than the six-membered ring, as formulated in ref. 7. Saponification of III prepared from VIII yielded the *cis*-acid, IV. Complete hydrogenation of VIII in acetic acid and sublimation of the product formed the saturated anhydride, V. Complete reduction of the *cis*-acid IX formed the saturated *cis*-acid VII, while reduction of the *trans*-acid X formed the saturated *trans*-acid, VI.

Assignment of *cis* configurations to the acids IV, VII and IX is based on their preparation from the anhydrides III, V and VIII, respectively, and their easy reconversion to the anhydrides by heating. A *trans* relationship of the carboxyl groups in VI and X is indicated by the fact that these acids do not form anhydrides on heating. The steric configurations of the rings in the series of compounds cannot be determined from the evidence that is available at present. The addition of bromine to VIII forming a monobromolactonic acid was formulated as proceeding through addition to the double bond in the six-membered ring, and the remaining double bond was stated to be inert to bromine.[7] However, in the partial reduction of VIII to III the four-membered ring is hydrogenated, and the product does not react readily with bromine. Accordingly it is possible that the bromolactone previously described has a lactone ring between the six- and four-membered rings, rather than the two six-membered rings.

Conclusive evidence of the presence of a four-membered ring in the Diels–Alder adducts of II (and I) was obtained by study of the adduct prepared from I and dimethyl acetylenedicarboxylate. The structure of the adduct was established as XI by quantitative hydrogenation with the absorption of two molar equivalents of hydrogen; saponification of the saturated ester yielded the *trans*-tetrahydro acid, VI. Pyrolysis of XI resulted in the formation of cyclobutene (95% yield) and dimethyl phthalate, the expected products according to the Alder–Rickert rule.[8] The cyclobutene was identified by comparison of its infrared spectrum with the spectrum of a sample prepared from cyclobutyldimethylamine oxide,[9] by conversion to a dibromide, and by oxidation to succinic acid. This sequence of reactions provides an advantageous route for the synthesis of cyclobutene.



XI

Experimental[10]

Preparation of a Mixture of 1,3,5-Cycloöctatriene (I) and Bicyclo[4.2.0]octa-2,4-diene (II) from Cycloöctatetraene.—Liquid ammonia (200 ml.) was condensed in a dry 500-ml. three-necked flask fitted with a Hershberg stirrer and an efficient water-cooled reflux condenser. A solution of 20.8 g. (0.20 mole) of cycloöctatetraene in 100 ml. of dry ether was added with cooling to −80° in a bath containing Dry Ice and acetone. Small pieces of freshly cut sodium (10.1 g., 0.44 gram atom) were added over a period of 20 minutes at −80°, and the mixture was stirred at that temperature for 30 minutes after the addition was completed. The sodium adduct was decomposed by addition of 26.8 g. of solid ammonium chloride during a period of 15 minutes, after which 100 ml. of ether was added and the ammonia was allowed to escape through the condenser. Water was added to the residue, and the organic phase was separated, washed with water until neutral, and dried over sodium sulfate. The ether was removed through a 16 × 1.0-cm. glass helix-packed column, and the residue was distilled rapidly in a nitrogen atmosphere, yielding 18.8 g. of a yellow mixture of hydrocarbons, b.p. 68–79° (60 mm.). The distillate was dissolved in an equal volume of pentane and washed with 50% (by weight) aqueous silver nitrate until the solution was colorless to remove cycloöctatetraene, with the addition of water when necessary to dissolve the crystalline cycloöctatetraene–silver nitrate complex. The pentane solution was washed with water, dried over sodium sulfate, and added to the potassium *t*-butoxide prepared from 0.1 g. of potassium and 20 ml. of *t*-butyl alcohol. The pentane was distilled and the residue was heated in a nitrogen atmosphere under reflux on a steam-bath for 1 hour, cooled, and poured into water. The organic phase was dissolved in pentane, washed with water until neutral, and dried over sodium sulfate. The pentane was removed through a 16 × 1.0-cm. glass helix-packed column, and the residue was distilled rapidly at 60 mm. under nitrogen, yielding 11.5 g. (51%) of a mixture of I and II, b.p. 70–73° (60 mm.), $n^{25}\mathrm{D}$ 1.5192 (containing 73% I and 27% II according to the refractive index).

1,3,5-Cycloöctatriene (I).—The silver nitrate complex of I, m.p. 125–126°, was prepared from mixtures of I and II by the procedure of ref. 3, p. 2518, or by the addition of a 10% excess of saturated aqueous silver nitrate (based on the amount of I present) to a 20% solution of the mixture in absolute ethanol. The complex was recrystallized from absolute ethanol, and decomposed by adding it to water and then adding concentrated ammonium hydroxide with stirring until the precipitate of silver hydroxide disappeared. The hydrocarbon was washed with water and dried by passing it through silica gel. The refractive index of pure I obtained in this way was 1.5249, and was not changed by rapid distillation at 0.5 mm. with a pot temperature below 40°.

Bicyclo[4.2.0]octa-2,4-diene (II).—Pure I was converted into a mixture of I and II by slow distillation through a 16 × 1.0-cm. glass helix-packed column at 85–86° (120 mm.). The distillate (6.72 g., containing 2.6 g. of II according to the refractive index) was added to a suspension of 7.0 g. (5% molar excess of the amount of I present) of finely powdered silver nitrate in 15 ml. of boiling absolute ethanol. The solution that was formed was cooled quickly to 0° with stirring and the crystalline silver nitrate complex of I was separated by centrifuging. The complex was washed with 10 ml. of cold absolute ethanol and the combined ethanol solutions were diluted with ice-water in a 100-ml. volumetric flask under nitrogen. The phases were allowed to separate for 30 minutes at 0°, after which the hydrocarbon layer was removed, and washed twice with water and six times with 0.2-ml. portions of 50% (by weight) aqueous silver nitrate. Any solid that separated was removed by centrifuging. The refractive index of the product (II) was unchanged by further extraction with 50% silver nitrate or by rapid distillation at 0.5 mm. with a pot temperature below 30°; $n^{25}\mathrm{D}$ 1.5035.

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.63; H, 9.81.

The separation of I and II also was effected by the following procedure. A saturated aqueous solution of 20.7 g. of silver nitrate was added with stirring to a solution of 17.85

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(8) K. Alder and H. F. Rickert, *Ann.*, **524**, 180 (1936).

(9) J. D. Roberts and C. W. Sauer, This Journal, **74**, 3192 (1952).

(10) Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

g. of a mixture of I and II (n^{25}D 1.5180, containing 11.8 g. of I according to the refractive index) in 100 ml. of absolute ethanol at 0 to 5°. The solution was allowed to stand for 30 minutes at 0°, and the crystalline silver nitrate complex of I (30.5 g.) was separated by filtration and the filtrate was diluted with 1 l. of ice-water. The crude II that separated (4.5 g., n^{25}D 1.5070) was purified by the procedure described above.

In quantitative hydrogenation of II in the presence of Adams platinum catalyst in acetic acid, 100–102% of two molar equivalents of hydrogen were absorbed. The reduction product, isolated by a procedure similar to one described in ref. 3, p. 2517, was identified as bicyclo[4.2.0]-octane by its infrared spectrum (absorption bands are listed in ref. 3, p. 2519); n^{25}D 1.4598, n^{20}D 1.4620 (lit. n^{20}D 1.4621,[5] 1.4613[7]).

Structures of 1,3,5-Cycloöctatriene (I) and Bicyclo-[4.2.0]octa-2,4-diene (II) by Oxidation.—Ozonization of I was conducted by introducing a stream of oxygen delivering 10 mg. of ozone per minute into a solution of 0.11 g. of I in 25 ml. of glacial acetic acid for 25 minutes at room temperature. The solution was heated with 5 ml. of 35% hydrogen peroxide for 2 hours at 100°. Removal of the solvent and sublimation of the residue at 0.3 mm. yielded 0.079 g. of crude succinic acid, m.p. 175–179°, which was recrystallized from absolute ethanol–pentane and identified by melting point and mixed melting point with an authentic sample.

Oxidation of II was accomplished most successfully with acidified permanganate; ozonization led to partial polymerization and consequently to the formation of mixtures. A solution of 0.28 g. of II in 50 ml. of acetone was added to 100 ml. of water containing 3 ml. of concentrated sulfuric acid. The solution was added to 2.3 g. of sodium permanganate trihydrate in 50 ml. of water, and after 10 minutes the mixture was warmed to 35–45°. Fifteen minutes later, when the permanganate was decolorized, an additional 1.6 g. of sodium permanganate trihydrate in 50 ml. of water was added, and the mixture was allowed to stand for 30 minutes at 35–45°, until the permanganate color disappeared. Sufficient solid sodium bisulfite was added to reduce the manganese dioxide, and the solution was concentrated to a volume of 25 ml. Concentrated hydrochloric acid (10 ml.) was added, and the solution was extracted with ether in a continuous extractor for 8 hours. The extract was concentrated, and the residue was purified by partition chromatography on wet silicic acid by the procedure of Marvel and Rands.[11] The chloroform–*n*-butanol effluent was collected in 25-ml. fractions, which were concentrated to dryness. Fraction no. 11 yielded 0.10 g. (39%) of cyclobutane *cis*-1,2-dicarboxylic acid, m.p. 129–136°, which after two crystallizations from a mixture of ether and pentane was analytically pure, had a melting point and mixed melting point with an authentic sample[12] of 136.5–138°, and had an infrared spectrum (Nujol mull) identical with the known sample.

Equilibration of 1,3,5-Cycloöctatriene (I) and Bicyclo-[4.2.0]octa-2,4-diene (II).—Samples of I (n^{25}D 1.5249) and II (n^{25}D 1.5035) were sealed in Pyrex tubes under nitrogen at about 30 mm. pressure and heated at 100° for 1 hour. Both samples remained colorless upon heating and changed in refractive index to n^{25}D 1.5216 (indicating a composition of 85% of I and 15% of II). The heated samples had identical infrared spectra that contained absorption bands characteristic of I and II (Fig. 2) and no additional bands.

The isolation of pure II from samples of I that had been heated to establish the equilibrium I $\rightleftarrows$ II (the preparation of II described above) establishes the fact that I is converted into II upon heating. Occurrence of the reverse reaction was established as follows. A 64-mg. sample of II was sealed in a Pyrex tube under nitrogen and heated at 100° for 18 minutes. The equilibrium mixture of I and II (n^{25}D 1.5218) thus obtained was added to a suspension of 85 mg. of finely powdered silver nitrate in 1 ml. of absolute ethanol, and the mixture was warmed until a clear solution was formed. Upon cooling the crystalline silver nitrate complex of I separated. It was recrystallized from absolute ethanol; yield 32 mg., m.p. 123–124.5°, which was not depressed on mixture with an authentic sample.

Reduction of Cycloöctatetraene Dibromide to a Mixture of I and II.—A solution in 50 ml. of dry tetrahydrofuran of the crude cycloöctatetraene dibromide prepared from 10.4 g. of cycloöctatetraene was added dropwise to a stirred solution of 11.4 g. of lithium aluminum hydride and 0.5 g. of sodium iodide in 100 ml. of tetrahydrofuran. The reaction temperature was maintained at 20–25° during the addition and while the mixture was stirred for an additional period of 1.5 hours. All of the mixture (about 120 ml.) that was volatile at room temperature and 1 mm. was removed by distillation, and the distillate was poured into a large volume of water. The organic layer was separated, washed, and dried. It amounted to 1.9 g. of a yellow liquid, n^{25}D 1.5140. The residue from distillation of the volatile product and solvent was allowed to stand at room temperature for 12 hours, after which repetition of the distillation and washing the distillate with water yielded an additional 5.3 g., n^{25}D 1.5172. The two fractions were combined and washed three times with 20% aqueous silver nitrate to remove cycloöctatetraene.[13] After this treatment 3.4 g. of mixture of I and II remained, n^{25}D 1.5200. Addition of 6.2 g. of saturated aqueous silver nitrate solution to a solution of the hydrocarbons in 10 ml. of absolute ethanol yielded 4.7 g. of the silver nitrate complex of I, m.p. and mixed m.p. with an authentic sample, 124–126°. Pure I (0.56 g.) was regenerated from 2 g. of the complex with ammonium hydroxide and identified by its refractive index (n^{25}D 1.5244) and comparison of its infrared spectrum with the spectrum of I prepared and purified by the methods described at the beginning of the Experimental part.

Diels–Alder Adducts Derived from I and II. Reaction of Bicyclo[4.2.0]octa-2,4-diene (II) with Maleic Ahhydride.—A solution of 143 mg. of II in 3 ml. of benzene was added dropwise to 96 mg. of maleic anhydride in 3 ml. of benzene at 10°, and the solution was allowed to stand at that temperature under nitrogen for 24 hours. Evaporation of the solvent in a stream of dry nitrogen yielded 199 mg. (98%) of the maleic anhydride adduct III, m.p. 140–143.5°. 1,3,5-Cycloöctatriene (I) and maleic anhydride failed to react in benzene at 10° during a period of 24 hours under the conditions described above for the reaction of II, and evaporation of the solvent yielded only the maleic anhydride.

Structure of the Maleic Anhydride Adduct III.—By comparison of melting points, mixed melting points and infrared spectra, III prepared from II was proved to be identical with the maleic anhydride adduct prepared from 1,3,5-cyclooctatriene (I) in boiling benzene, m.p. 144–145°,[3,14] and with the dihydro derivative of the cycloöctatetraene–maleic anhydride adduct described below.

The anhydride III was hydrolyzed by adding 10% sodium hydroxide to a suspension of 0.54 g. of III in 15 ml. of boiling water until a clear solution was obtained. Acidification with hydrochloric acid precipitated the *cis*-acid IV, which was dried under reduced pressure at room temperature; yield 0.50 g., m.p. 161–162° (introduced at 150° and heated 2° per minute). The anhydride III was formed from IV at the melting point.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.85; H, 6.47.

A solution presumed to contain the mono- and diethyl esters of IV was prepared by warming 1.50 g. of the anhydride with 15 ml. of absolute ethanol containing 2 drops of concentrated hydrochloric acid until the solid dissolved, and diluting to 25 ml. with ethanol. A 9.9-ml. aliquot (corresponding to 0.59 g. of III) was added to 5 ml. of glacial acetic acid containing 0.1 g. of prereduced platinum oxide and hydrogenated. Hydrogen absorption was completed in 80 minutes and amounted to 100% of one molar equivalent. After separation of the catalyst and concentration of the filtrate to one-fourth of the original volume, the residue was heated overnight on a steam-bath with 35 ml. of 5% sodium hydroxide. The solution was cooled, acidified to congo red with hydrochloric acid, and the acid that separated was crystallized from acetic acid (10 ml.) and water (20 ml.). The mixture of acids obtained (0.31 g., m.p. 165–215°) was

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[11] C. S. Marvel and R. D. Rands, Jr., This Journal, **72**, 2642 (1950).

[12] Kindly furnished by Dr. E. R. Buchman; E. R. Buchman, A. O. Reims, T. Skei and M. J. Schlatter, *ibid.*, **64**, 2696 (1942).

[13] Formation of some cycloöctatetraene would be expected from the reaction of cycloöctatetraene dibromide and sodium iodide; see R. E. Benson and T. L. Cairns, *ibid.*, **72**, 5355 (1950). Cycloöctatetraene itself is not reduced readily by lithium aluminum hydride (unpublished observation of F. A. Hochstein).

[14] A. C. Cope, H. R. Nace and L. L. Estes, Jr., *ibid.*, **72**, 1123 (1950).

sublimed at 120° and 2 mm., and yielded 0.19 g. of the volatile anhydride V, which after resublimation had a melting point and mixed melting point with the tetrahydro derivative of the cycloöctatetraene–maleic anhydride adduct described below of 133–134°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.90; H, 6.84. Found: C, 69.76; H, 6.98.

The residue from the sublimation of V was 0.12 g. of the *trans*-acid VI, which was purified by dissolving it in dilute sodium hydroxide and reprecipitating with hydrochloric acid; m.p. and mixed m.p. with the tetrahydro *trans*-acid derived from the cycloöctatetraene–maleic anhydride adduct described below, 234–236° (dec.).

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.28; H, 7.19. Found: C, 64.42; H, 7.32.

The saturated anhydride V described above was hydrolyzed (under the conditions used for hydrolysis of III) to the saturated *cis*-acid VII, melting point and mixed melting point with the tetrahydro *cis*-acid derived from the cyclooctatetraene–maleic anhydride adduct 167–168° (with formation of the anhydride V at the melting point).

Samples for comparison with the acids and anhydrides III to VII were prepared from the cycloöctatetraene–maleic anhydride adduct (VIII), obtained by the procedure of ref. 7, p. 66, by heating the reactants under dry nitrogen at 170°. The adduct VIII was isolated by sublimation under reduced pressure, and separated in that manner from approximately 5% of a non-volatile product not previously described. This material was insoluble in common solvents, melted at 380° (dec., sealed tube), dissolved slowly in dilute sodium hydroxide and was recovered essentially unchanged by acidification and drying. It appeared to be polymeric, but elementary analysis corresponded approximately to the formula $(C_{21}H_{20}O_6)_n$ (Calcd.: C, 68.46; H, 5.47. Found: C, 68.74; H, 5.40) rather than to any simple copolymer of cycloöctatetraene and maleic anhydride.

Reduction products of the cycloöctatetraene–maleic anhydride adduct VIII were prepared as follows. The dihydro anhydride III was obtained by dissolving VIII in dilute potassium hydroxide, hydrogenating in the presence of 10% palladium-on-Norit until 102% of one molar equivalent of hydrogen was absorbed, acidifying and subliming the precipitated acid at 120° and 0.5 mm.; m.p. 144–145°. Hydrolysis of III from this source gave the *cis*-acid IV, m.p. 155–155.5°, with formation of III at the melting point. Hydrogenation of VIII in acetic acid in the presence of Adams platinum catalyst resulted in the absorption of two molar equivalents of hydrogen, and sublimation of the product yielded the tetrahydro anhydride V, m.p. 132–134°. The *cis*-tetrahydro acid, VII, was prepared by dissolving the anhydride VIII in dilute sodium hydroxide and hydrogenating in the presence of 10% palladium-on-Norit. Two molar equivalents of hydrogen was absorbed, and acidification of the solution yielded the *cis*-tetrahydro acid V, m.p. 168.5–169.5° (with formation of the anhydride at the melting point). The *trans*-tetrahydro acid VII was prepared by the procedure of ref. 7, p. 74, by converting the anhydride VIII to the dimethyl ester of the corresponding acid (IX), isomerizing to the *trans*-dimethyl ester by heating with sodium methoxide in methanol, and saponifying to the *trans*-acid X, m.p. 223–224.2°. Hydrogenation of X in glacial acetic acid in the presence of Adams platinum catalyst yielded the *trans*-tetrahydro acid VI, m.p. 232.8–234.4°.

Diels-Alder Adduct of Cycloöctatriene and Dimethyl Acetylenedicarboxylate (XI).—1,3,5-Cycloöctatriene was regenerated from 10.0 g. (0.0362 mole) of the silver nitrate complex with ammonium hydroxide, taken up in benzene, and dried over silica gel. The solution was added to 7.0 g. (0.061 mole) of dimethyl acetylenedicarboxylate and heated under nitrogen at 60° for 24 hours. The solvent was distilled under reduced pressure, followed by removal of excess dimethyl acetylenedicarboxylate by warming at 60° at a pressure of 0.05 mm. for 8 hours. The residual adduct (7.19 g., 77%) was distilled in a short path still at 105° (0.2 mm.); $n^{25}D$ 1.5145.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.91; H, 6.51.

Hydrogenation of a solution of 0.316 g. of the adduct XI in ethanol in the presence of 10% palladium-on-Norit resulted in the absorption of 97% of two molar equivalents of hydrogen. The saturated ester that was formed was saponified by boiling for 6 hours with 10% potassium hydroxide. The acid that was isolated after cooling and acidifying in a yield of 0.237 g. (83%) was recrystallized once from methanol and water, and proved to be the *trans*-tetrahydro acid VI, m.p. and mixed m.p. with a sample described above derived from VIII, 234–236°.

Formation of Cyclobutene from the Adduct XI.—The adduct XI (4.72 g.) was placed in a 5-ml. flask with a capillary inlet attached to a source of dry nitrogen. The flask was connected to a 25-cm. tube that served as an air-cooled condenser, which led to a trap cooled with liquid nitrogen. The system was evacuated to 100 mm., and the flask was heated in a bath at 200° for 20 minutes. The flask was cooled and nitrogen was admitted. The trap contained 0.97 g. (95%) of cyclobutene, which was solid at the temperature of liquid nitrogen and liquefied when placed in a Dry Ice-bath at −80°. The cyclobutene was identified by comparison of its infrared spectrum with the spectrum of an authentic sample prepared from cyclobutyldimethylamine oxide,[9] by conversion to the dibromide, and by oxidation with neutral aqueous sodium permanganate to succinic acid, m.p. and mixed m.p. with an authentic sample, 184–185°. The residue from the pyrolysis of XI was shown to be dimethyl phthalate by comparison of its infrared spectrum with the spectrum of an authentic sample, and by saponification to phthalic acid, isolated by sublimation as phthalic anhydride.

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