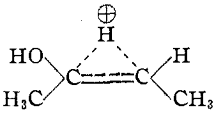
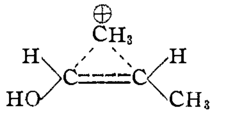
ethyl ketone is almost the exclusive product. From the *meso* diol, however, structure XXI would be a more stable ion or transition state than XX on the basis of steric considerations alone.


XX


XXI

If, however, the combined rates of hydride group migration and elimination are intrinsically more rapid than the migration of a methyl group, the effects would balance out against each other and a mixture of products would be expected.

Of these two interpretations, we prefer the second since it would seem that rotation about the central carbon–carbon bond in such a simple molecule as a 2,3-butanediol should proceed faster than rearrangement. We feel, however, that the alternative explanation should not be discarded until more experiments have been performed.

The fact that the *cis* and *trans* epoxides gave, within the limits of experimental error, the same proportions of aldehyde and ketone as did the *dl* and *meso* diols, suggests that these reactions involve the same intermediate. It is likely that for both reactions the glycols are the species which actually undergo rearrangement and that the first step in the epoxide rearrangement is simply hydrolysis to the *dl* and *meso* glycols, respectively.[20]

It is not yet clear why less isobutyraldehyde should be formed by the action of silver nitrate on the 3-chloro-2-butanols than from the pinacol rearrangement of the 2,3-butanediols. Seemingly essentially the same transition states should be involved and any steric effects of the large silver ion would appear to be in the direct forcing the methyl group on the adjacent carbon atom nearer the backside of the chlorine atom. This would be expected to result in the formation of more rather than less isobutyraldehyde, but is not in accord with fact. An alternative explanation, namely, that the isobutyraldehyde is oxidized by the nitric acid formed during the reaction, was not supported by experiment. Under the conditions of the experiment, treatment of isobutyraldehyde with the same amount of nitric acid as would be formed during the rearrangement caused no oxidation or consumption of the aldehyde.

[20] See Wheland, ref. 2, pp. 470–473.

URBANA, ILLINOIS RECEIVED JULY 7, 1950

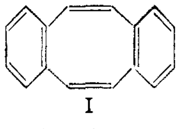
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

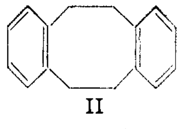
Cyclic Polyolefins. XIV. 3,7-Dibromo-1,2,5,6-Dibenzcycloöctadiene and 1,2,5,6-Dibenzcycloöctatetraene

BY ARTHUR C. COPE AND STUART W. FENTON

The hydrocarbon 1,2,5,6-dibenzcycloöctadiene (II), previously described by Baker, Banks, Lyon and Mann, has been prepared in an improved yield of 30–46% from α,α′-dibromo-*o*-xylene and sodium under conditions of high dilution Bromination of II with N-bromosuccinimide formed 3,7-dibromo-1,2,5,6-dibenzcycloöctadiene (III) in 70–90% yield. The structure of III was established by conversion to the diol IV by direct hydrolysis, or better through preparation and hydrolysis of the diacetate V, followed by oxidation of IV to 3-hydroxy-1,2,5,6-dibenzcycloöctadien-7-one hemiketal (VII). The structure of VII was determined by comparison with an identical sample obtained by the Meerwein–Ponndorf reduction of 1,2,5,6-dibenz-1,5-cycloöctadiene-3,7-dione (VIII), prepared by the procedure of Wawzonek. Pyrolysis of the diacetate V resulted in the elimination of two equivalents of acetic acid and the formation of 1,2,5,6-dibenzcycloöctatetraene (I) in 70% yield. The hydrocarbon I obtained by this route was identified by reduction to II, and by direct comparison with a sample prepared by the longer original synthesis of I described by Fieser and Pechet.

The synthesis of 1,2,5,6-dibenzcycloöctatetraene (I) by a reaction sequence beginning with the condensation of *o*-phthalaldehyde and *o*-phenylenediacetonitrile has been described by Fieser and Pechet.[1] 1,2,5,6-Dibenzcycloöctadiene (II) has been prepared in 5–6% yield from α,α′-dibromo-*o*-xylene and sodium in dioxane by Baker, Banks, Lyon and Mann.[2] If II could be prepared in better yield, it might be useful as an intermediate in the synthesis of I and other derivatives of cycloöctatetraene. This paper reports an investigation of these possibilities.


I


II

The yield of II obtained from α,α′-dibromo-*o*-xylene and sodium was found to be dependent upon the concentration (Fig. 1). With the most dilute solution of the dibromide in dioxane that was studied the yield was 46%, but it was more economical of time and materials to use a simple high-dilution apparatus for the reaction, a procedure which formed II in a yield of 30%. The hydrocarbons 1,2,5,6,9,10-tribenz-1,5,9-cyclododecatriene and 1,2-di-(*o*-tolyl)-ethane, previously described as by-products of this reaction,[2] also were isolated. An examination of the lower boiling fractions gave no evidence that 1,2-benz-1-cyclobutene was present.

The reaction of 1,2,5,6-dibenzcycloöctadiene (II) with one molar equivalent of N-bromosuccinimide proceeded readily but no monobromide was isolated from the product, which proved to be a mixture of a dibromide III and unchanged II. With two molar equivalents of N-bromosuccinimide a 70–90% yield of the dibromide (later proved to be 3,7-dibromo-1,2,5,6-dibenz-1,5-cycloöctadiene

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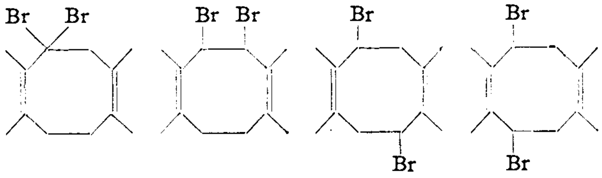
[1] L. F. Fieser and M. M. Pechet, THIS JOURNAL, **68**, 2577 (1946).

[2] W. Baker, R. Banks, D. R. Lyon and F. G. Mann, *J. Chem. Soc.*, 27 (1945).

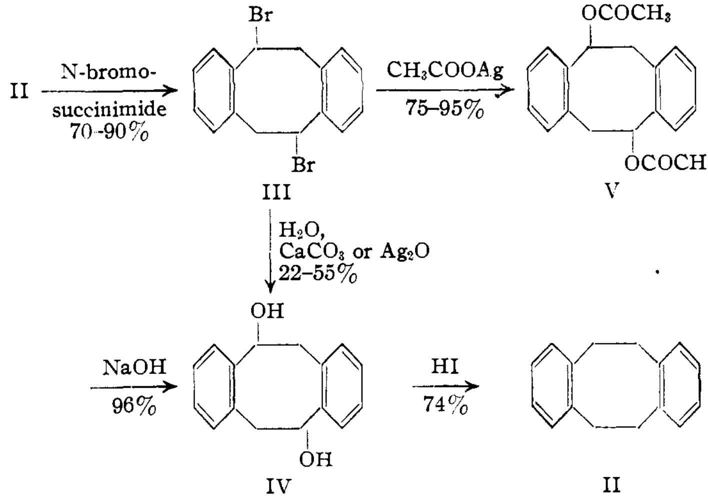
(III)) was obtained. Proof that no rearrangement of the carbon skeleton had occurred in the bromination was furnished by reduction of III with sodium in liquid ammonia, which yielded the original hydrocarbon II.

Excluding possible geometric isomers and isomers containing bromine in the benzenoid rings, the dibromide derived from II could be any one of the four position isomers represented by partial formulas IIIa–IIId.



IIIa IIIb IIIc IIId

Evidence that structure IIIb was not the correct one was obtained by treating III with sodium iodide in acetone, which resulted in partial replacement of the bromine by iodine rather than the elimination of halogen with the formation of another double bond. The dibromide III was hydrolyzed to a diol IV by heating with an aqueous suspension of silver oxide or calcium carbonate, thus excluding structure IIIa, which would be expected to form a ketone under these conditions. The yield of IV obtained by hydrolysis was low (22–55%), and a better route to IV was found in the reaction of III with silver acetate in glacial acetic acid, which formed the diacetate V in 75–95% yield. Saponification of the diacetate formed the diol in 96% yield. Evidence that there was no rearrangement of the carbon skeleton in this series of transformations was obtained by reduction of the diol IV with hydriodic acid in acetic acid, which reformed the original hydrocarbon II. The diol IV was not cleaved by lead tetraacetate in acetic acid, additional negative evidence against structure IIIb for the dibromide.



Evidence distinguishing between the remaining possible structures IIIc and IIId for the dibromide was obtained by oxidation of the glycol IV. Oxidation with chromium trioxide in glacial acetic acid formed an acidic and a neutral product. The acid proved to be 1-hydroxy-1,2-diphenylethane-*o*,*o*'-dicarboxylic acid lactone (VI), previously described by Ephraim.[3] Evidence for the structure of VI was obtained from its analysis, neutral equivalent, saponification equivalent, melting point and mixed melting point with a known sample prepared by a method similar to the one described by Ephraim. This oxidation product could be derived from either glycol structure IVc or IVd (corresponding to dibromide structures IIIc and IIId), and accordingly was not helpful in distinguishing between these possible formulas for III.

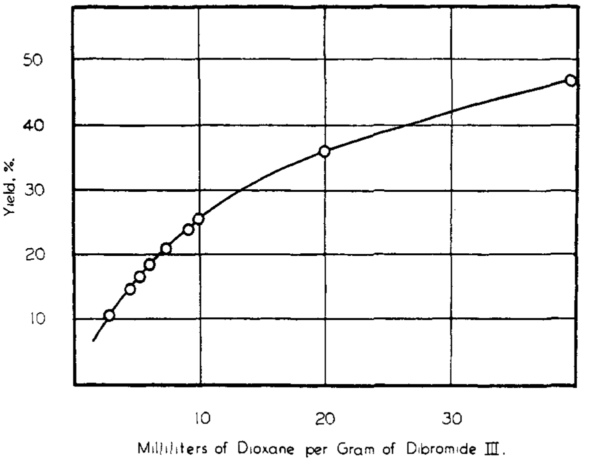
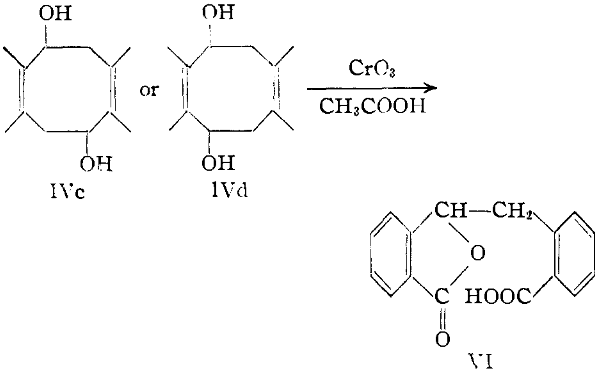


Fig. 1.—Effect of concentration on the yield of 1,2,5,6-dibenzcycloöctadiene (II).



The neutral oxidation product VII was also obtained from IV in higher (90%) yield by an Oppenauer oxidation with cyclohexanone and aluminum isopropoxide in benzene. From the molecular formula ($C_{16}H_{14}O_2$) of VII, and the fact that it was derived from a glycol with a structure corresponding to either IVc or IVd, five possible structures (partial formulas VIIa–VIIe) were considered. The infrared spectrum of VII (Fig. 2) contained a strong band at 3.0 μ indicating the presence of a hydroxyl group but no band in the 5–6 μ region in which absorption due to the presence of a carbonyl group should occur, and accordingly excluded structures VIIa and VIIc. A Zerewitinoff determina-

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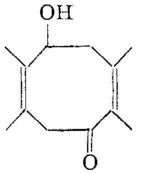
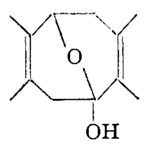
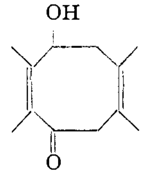
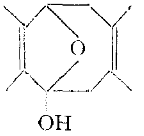
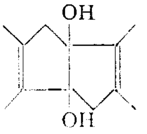
[3] J. Ephraim, *Ber.*, **24**, 2820 (1891). This compound may have either a γ- or a δ-lactone structure.


VIIa


VIIb


VIIc


VIId


VIIe

tion showed that only one active hydrogen was present and therefore excluded structure VIIe. Attempts to distinguish between the remaining possibilities by oxidation to a diketone which could be compared with 1,2,5,6-dibenz-1,5-cyclooöctadiene-3,7-dione (VIII), previously described by Wawzonek,[4] were unsuccessful.

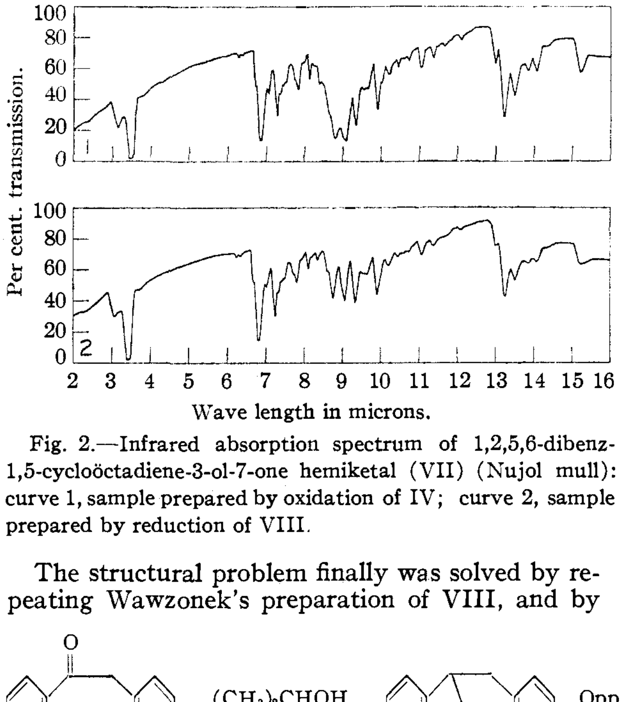
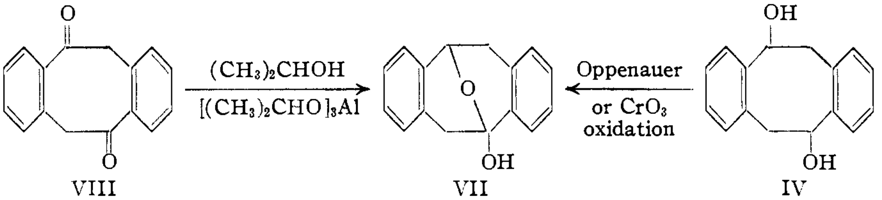


Fig. 2.—Infrared absorption spectrum of 1,2,5,6-dibenz-1,5-cyclooöctadiene-3-ol-7-one hemiketal (VII) (Nujol mull): curve 1, sample prepared by oxidation of IV; curve 2, sample prepared by reduction of VIII.

The structural problem finally was solved by repeating Wawzonek's preparation of VIII, and by reducing VIII by the Meerwein–Ponndorf method with isopropyl alcohol and aluminum isopropoxide. The product formed proved to be VII. Its identity with the oxidation product derived from IV was established by comparison of melting points, mixed melting point and infrared spectra (Fig. 2). Proof of the structure of VII permits the assignment of structure IV to the glycol and III to the dibromide.



VIII VII IV

Attempts to prepare 1,2,5,6-dibenzcyclooöctatetraene (I) from the dibromide III by dehydrobromination were unsuccessful because of a molecular rearrangement which is described in the following paper. Attempts to convert 1,2,5,6-dibenzcyclooöctadiene (II) to I by dehydrogenation through treatment with sulfur, chloranil, or palladium-on-carbon also were unsuccessful; in each case II was recovered. However, pyrolysis of the diacetate V at 500° resulted in the elimination of two equivalents of acetic acid and the formation of 1,2,5,6-dibenzcyclooöctatetraene (I) in 70% yield. The identity of I prepared by this route was proved by quantitative hydrogenation in the presence of a palladium catalyst to II, and by comparison with a sample of I prepared by the method of Fieser and Pechet.[1] Repetition of their synthesis provided a sample of I which was proved to be identical with I prepared by the pyrolysis of V by comparison of melting points, mixed melting point and infrared spectra (Fig. 3). The sample prepared by this route[1] also was characterized by ozonization followed by oxidation of the ozonide with hydrogen peroxide and then by sublimation, which formed phthalic anhydride in 83% yield. The preparation of I from α,α'-dibromo-*o*-xylene through the reactions: $\xrightarrow{30\%}$ II $\xrightarrow{70-90\%}$ III $\xrightarrow{75-95\%}$ V $\xrightarrow{70\%}$ I is shorter and furnishes a higher over-all yield than the original synthesis of this hydrocarbon.

Experimental[5]

1,2,5,6-Dibenz-1,5-cyclooöctadiene (II). **α,α'-Dibromo-*o*-xylene** was prepared from 212 g. of *o*-xylene and 704 g. of bromine by the procedure of Perkin,[6] except that the reaction temperature was maintained at 120° with an oil-bath and the mixture was irradiated with a General Electric 275 watt sun lamp at a distance of 5 cm. After one crystallization from 95% ethanol, the product amounted to 326 g. (61%) and melted at 90.5–91.8°. The compound is a lachrymator and the preparation and crystallization were conducted in a hood.

The preparations of II in yields which are shown graphically in Fig. 1 were conducted by the following modification of the procedure previously described.[2] These preparations differed from one another only in the volume of solvent.

A solution of 33.0 g. (0.125 mole) of α,α'-dibromo-*o*-xylene in 1320 ml. of dry dioxane was heated under reflux for 48 hours with 7.0 g. (0.304 gram atom) of sodium which previously had been powdered under toluene. The reaction mixture became bright blue in color. The solvent was distilled at atmospheric pressure, and the residue was dissolved in 250 ml. of benzene. The excess sodium was destroyed by cautious addition of 95% ethanol, and the benzene solution was washed with water and steam distilled.[7] After the benzene had distilled the receiver was changed, and the product collected as crystals in the condenser and receiver while 20–25 l. of water was distilled. The product was separated from the water and the portion in the condenser was removed by dissolving it in boiling 95% ethanol. Recrystallization from 95% ethanol yielded 5.98 g. (46%) of

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[4] S. Wawzonek, This Journal, **62**, 745 (1940).

[5] 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.

[6] W. H. Perkin, Jr., *J. Chem. Soc.*, **53**, 5 (1888).

[7] Apparatus suitable for rapid steam distillation described in Fieser, "Experiments in Organic Chemistry," second ed., D. C. Heath and Co., Boston, Mass., 1941, p. 320, was used except that a Friedrichs condenser was employed. The 2-l. flask used for distillation was heated with an electric mantle and from above with two infrared lamps (to reduce foaming).

II as colorless prisms melting at 108.5–109°. Sublimation at 0.2 mm. with a heating block temperature of 100–125° and recrystallization from 95% ethanol raised the melting point to 109.4–109.9° (lit. 108.5–110°,[1] 108.5°[2]) and the recovery was 93%.

The residue from the steam distillation was dried and sublimed at 0.15 mm. with a heating block temperature of 280°. The solid sublimate after several crystallizations from 95% ethanol formed long colorless needles of 1,2,5,6,-9,10-tribenz-1,5,9-cyclododecatriene, m.p. 183.5–184.5° (lit.[2] 184.5°). In an early preparation a small amount of 1,2-di-(*o*-tolyl)-ethane was isolated, as it was in the previous work; m.p. 56–58°. Fractional distillation of the low boiling hydrocarbons yielded only the benzene solvent and a small amount of *o*-xylene.

Larger amounts of II were prepared more conveniently by addition of a solution of 66 g. (0.25 mole) of α,α'-dibromo-*o*-xylene in 250 ml. of dry dioxane through a simple high-dilution apparatus to 14 g. (0.608 gram atom) of sodium (previously powdered under toluene) in 250 ml. of dry, refluxing dioxane. The high-dilution apparatus consisted of a still head attached to a reflux condenser which returned the dioxane to the flask through a U-tube. A side arm of the U-tube was connected to a Hershberg dropping funnel, through which the solution of the dibromide was added (during a period of 24 hours), so that it was diluted with solvent returning from the reflux condenser before entering the reaction flask. The mixture was heated under reflux for 24 hours after completion of the addition, and the product was isolated by the procedure described above. The yield of II was 7.8 g. (30%), m.p. 108.5–109°.

3,7-Dibromo-1,2,5,6-dibenz-1,5-cycloöctadiene (III).—A solution of 20.8 g. (0.1 mole) of II in 250 ml. of carbon tetrachloride was heated under reflux for one hour with 37.4 g. (0.21 mole) of N-bromosuccinimide. The mixture was cooled and filtered to separate succinimide, and the filtrate was concentrated under reduced pressure. The colorless, crystalline solid which precipitated was collected on a filter, washed thoroughly with water, and then dried under reduced pressure. It amounted to 32.1 g. (88%) of III, m.p. 187–188°. An analytical sample was purified by sublimation at 0.1 mm. with a heating block temperature of 185°, followed by recrystallization from 95% ethanol; m.p. 188.1–189°. Several preparations of III by this procedure gave yields varying from 70 to 90%.

Anal. Calcd. for $C_{16}H_{14}Br_2$: C, 52.49; H, 3.85; Br, 43.66. Found: C, 52.43; H, 3.95; Br, 43.55.

When III was prepared from 2.08 g. of II and 1.8 g. of N-bromosuccinimide (equimolecular quantities) under similar conditions, III was obtained in 27% yield and 41% of II was recovered.

The reduction of III to II was conducted by addition of a slurry of 1.0 g. of III in 30 ml. of dry ether to a solution of 1.0 g. of sodium in 175 ml. of liquid ammonia. The mixture was stirred for 15 minutes, solid ammonium chloride was added to destroy excess sodium, and the ammonia was allowed to evaporate. After addition of 100 ml. of water to the residue, the product was separated by extraction with methylene chloride. The solvent was distilled, and the product was isolated by sublimation at 0.3 mm. with a heating block temperature of 130°. The yield of II was 0.348 g. (61%), m.p. 108.5–109.5° and mixed melting point with an authentic sample 108.6–109.8°.

1,2,5,6-Dibenz-1,5-cycloöctadiene-3,7-diol Diacetate (V).—A mixture of 20 g. of III, 20 g. of silver acetate and 200 ml. of glacial acetic acid was heated under reflux for four hours. The precipitated silver bromide was removed by filtration, and the filtrate was added to a mixture of 500 g. of ice and 500 ml. of water with vigorous stirring. The colorless, finely divided solid which separated was collected on a filter, dried, and sublimed at 0.1 mm. with a heating block temperature of 180°. The crystalline sublimate was recrystallized from 95% ethanol and yielded 13.9 g. (78.5%) of V melting at 146.3–147°. An analytical sample which was recrystallized from 95% ethanol had the same melting point. Other preparations gave yields in the range of 75 to 95%.

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.05; H, 6.22. Found: C, 74.23; H, 6.27.

1,2,5,6-Dibenz-1,5-cycloöctadiene-3,7-diol (IV).—A solution of 1.00 g. of V and 0.25 g. of sodium hydroxide in 50 ml. of 95% ethanol was heated under reflux for three hours. Addition of 100 ml. of water precipitated IV as colorless crystals, which were collected on a filter after the mixture had stood at 5° for ten hours. The yield of IV after drying was 0.715 g. (96%), m.p. 213.8–215.7°. Two crystallizations from ethyl acetate yielded 0.69 g. (93%) of IV, m.p. 214.8–216°.

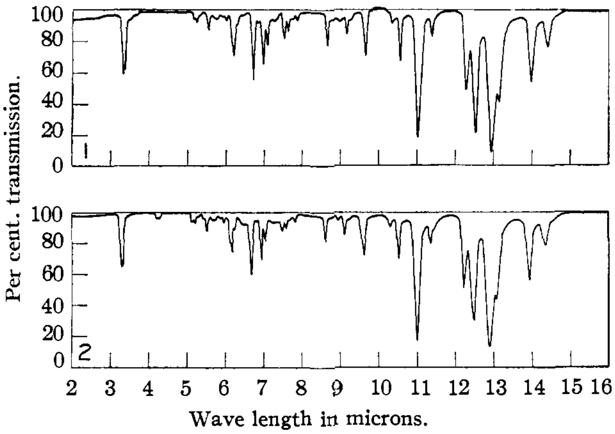

Fig. 3.—Infrared absorption spectrum of 1,2,5,6-dibenzcycloöctatetraene (I): curve 1, sample prepared by pyrolysis of V; curve 2, sample prepared by the method of Fieser and Pechet.[1] The spectra were determined for 10% solutions in carbon tetrachloride in the region 2–12 μ and for 10% solutions in carbon disulfide in the region 12–16 μ.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.18; H, 7.03.

The diol IV was also prepared from the dibromide III by direct hydrolysis, although the procedure in which V is prepared as an intermediate is preferred. A mixture of 0.1 g. of III, 25 ml. of water and 1 g. of calcium carbonate was heated under reflux for 48 hours; the yield of IV was 22%. Treatment of III with an aqueous suspension of silver oxide under similar conditions formed IV in 55% yield. In both cases some III remained unchanged.

No oxidation appeared to occur when a solution of IV and lead tetraacetate in glacial acetic acid was allowed to stand for one week at room temperature, and unchanged IV was recovered in 60% yield.

The reduction of IV to II was accomplished by heating 0.50 g. of IV with 10 ml. of 57% hydriodic acid and 100 ml. of glacial acetic acid under reflux for two hours. The mixture was cooled, diluted with 250 ml. of water, and made basic with ammonium hydroxide. The colorless solid which separated was extracted with methylene chloride. The extracts were washed with aqueous sodium bisulfite to remove iodine, concentrated, and the residue was sublimed at 0.5 mm. with a heating block temperature of 120°. The crystalline sublimate of II was recrystallized three times from 95% ethanol, and then amounted to 324 mg. (74%), m.p. 109–109.5° and mixed melting point with a known sample 109.2–109.7°.

Chromic Acid Oxidation of IV.—A solution of 0.555 g. of chromium trioxide in 25 ml. of glacial acetic acid was added dropwise with stirring during a period of 1.5 hours to a solution of 1.00 g. of IV in 50 ml. of glacial acetic acid. The solution was stirred for an additional period of three hours, diluted with 300 ml. of water, and extracted with four 100-ml. portions of methylene chloride. The combined extracts were washed twice with water, and then extracted with three 50-ml. portions of 10% aqueous sodium carbonate to separate the acidic product. The basic extracts were acidified with dilute hydrochloric acid, and the colorless solid which separated was extracted with methylene chloride. A colorless solid which was obtained by distillation of the solvent was sublimed at 0.3 mm. with a heating block temperature of 180–200°. The product amounted to 0.228 g. and melted at 201–202.5°. Recrystallization from 95% ethanol yielded an analytical sample of 1-hydroxy-1,2-diphenylethane-*o*,*o*'-dicarboxylic acid lactone (VI), melting point and mixed melting point with a known sample described below 201.5–202.5°.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51; neut.

equiv., 268; sapon. equiv., 134. Found: C, 71.61; H, 4.62; neut. equiv., 264; sapon. equiv., 129.

On distillation of the methylene chloride from the solution from which VI had been extracted a solid was obtained, which was sublimed at 0.3 mm. with a heating block temperature of 170°. The pale yellow sublimate (0.501 g.) was crystallized twice from 95% ethanol, and yielded colorless crystals of 1,2,5,6-dibenz-1,5-cycloöctadiene-3-ol-7-one hemiketal (VII) melting at 178.3–179.3°. A mixed melting point of VII from this source with a known sample prepared from VIII was 178.4–179.8°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92; active hydrogen, 1.00 equiv. Found: C, 80.55; H, 5.91; active hydrogen, 0.96 equiv.

Oppenauer Oxidation of IV.—A solution of 1.0 g. of IV, 6.0 g. of cyclohexanone and 1.0 g. of freshly prepared aluminum isopropoxide in 50 ml. of dry benzene was heated under reflux for 12.5 hours. The mixture was cooled, 100 ml. of 20% hydrochloric acid was added, and the benzene layer was separated, washed with water and dried over sodium sulfate. The benzene was distilled and the crystalline residue was sublimed at 0.1 mm. with a heating block temperature of 150°. The sublimate was recrystallized from 95% ethanol, and yielded 0.90 g. (91%) of VII, m.p. 176–178°. Two recrystallizations from 95% ethanol yielded pure VII, m.p. 178.9–180.5° and mixed m.p. with a known sample prepared from VIII 179.4–180.6°.

1-Hydroxy-1,2-diphenylethane-*o,o'*-dicarboxylic Acid Lactone (VI).—**Desoxybenzoin-2,2'-dicarboxylic acid** was prepared by the method described by Ephraim[3] from 10 g. of homophthalic acid, 10 g. of phthalic anhydride and 1.0 g. of sodium acetate. The product after crystallization from glacial acetic acid was obtained in a yield of 5.5 g. (26%), m.p. 241–243° (lit. 238–239°[3] and 215–245°[4]). A solution of 2.84 g. of desoxybenzoin-2,2'-dicarboxylic acid in 250 ml. of water containing 2 g. of sodium hydroxide was hydrogenated in the presence of 2 g. of W-7 Raney nickel[8] at 25° and atmospheric pressure. Hydrogen absorption was quantitative and required a period of eight hours for completion. The catalyst was removed by filtration, and the filtrate was acidified with dilute hydrochloric acid. The solid product was collected on a filter, dried, and recrystallized from 95% ethanol. The lactone VI was obtained as colorless crystals melting at 201.5–202.5° (lit.[3] 201°) in a yield of 2.65 g. (93%). When VI was prepared by reduction with sodium amalgam[3] a less pure product was obtained in poorer yield.

1,2,5,6-Dibenz-1,5-cycloöctadiene-3,7-dione (VIII).—*sym*-Diphenylsuccinonitrile was prepared from α-phenylcinnamonitrile[9] (20.5 g.) according to the procedure of Lapworth and McRae[10] as modified by Brand and Loehr.[11] The yield was 22.5 g. (98%) of a product which melted at 223–225° without recrystallization.

***sym*-Diphenylsuccinic acid** was prepared by the method of Lapworth and McRae[10] from 70 g. of *sym*-diphenylsuccinonitrile and obtained in a yield of 65.4 g. (80%) after purification through its sodium salt; m.p. 227–229°.

9,12-Diphensuccindanedione was prepared by a modification of a procedure described by Roser.[12] *sym*-Diphenylsuccinic acid (20 g.) was added with stirring to 160 g. of concentrated sulfuric acid at 110°. The acid dissolved rapidly forming a black solution, and as soon as solution was complete (ten minutes) the mixture was poured into ice and water. The colorless solid which separated was collected on a filter, dried, and crystallized from 95% ethanol as colorless crystals which were obtained in a yield of 5.2 g. (30%), m.p. 203.5–205°. At a reaction temperature of 130°[12] the yield of 9,12-diphensuccindanedione was very small.

9,12-Dichloro-9,11-diphensuccindadiene was prepared by the method of Wawzonek[4] from 20 g. of 9,12-diphensuccindanedione in a yield of 15.1 g. (65%) as dark red needles, m.p. 190.8–191.8°.

10-Diphensuccindene was prepared by a procedure suggested by the work of Brand and Müller.[13] An excess of zinc dust (5 g.) was added slowly to a mixture of 0.5 g. of 9,12-dichloro-9,11-diphensuccindadiene and 20 ml. of glacial acetic acid at the reflux temperature. When the brilliant red color was discharged, the nearly colorless reaction mixture was cooled, and the acetic acid solution was decanted (to separate excess zinc) into 100 g. of ice and 100 ml. of water. The colorless solid which precipitated was extracted with 100 ml. of ether, and the extract was washed with water and concentrated. The pale yellow, crystalline residue was washed with a small volume of cold ether and dried. The 10-diphensuccindene obtained amounted to 0.34 g. (91%), and melted at 205–208° (lit.[4] 204–208°). Recrystallization from ethyl acetate did not raise the melting point.

1,2,5,6-Dibenz-1,5-cycloöctadiene-3,7-dione (VIII) was prepared by a modification of the procedure described by Wawzonek.[4] A solution of 0.50 g. of 10-diphensuccindene in 35 ml. of ethyl acetate was treated with a stream of oxygen and ozone delivering 10 mg. of ozone per minute for 15 minutes at 0°. The ozonide was hydrogenated at room temperature and atmospheric pressure in the presence of 0.1 g. of 10% palladium-on-carbon in a period of 2 hours. The catalyst was separated by filtration, the solvent distilled, and the solid residue was sublimed at 0.5 mm. with a heating block temperature of 130°. The pale yellow solid sublimate, m.p. 198–202°, was crystallized twice from 95% ethanol, and yielded 179.3 mg. (31%) of VIII, m.p. 202–203° (lit.[4] 203.5–204.5°).

1,2,5,6-Dibenz-1,5-cycloöctadiene-3-ol-7-one Hemiketal (VII).—A solution of 0.15 g. of the diketone VIII and 1.0 g. of aluminum isopropoxide in 50 ml. of dry isopropyl alcohol was distilled slowly. Samples of the distillate were tested periodically with 2,4-dinitrophenylhydrazine reagent until the test for acetone was negative (30 minutes). The remainder of the solvent was distilled, and the residue was treated with sufficient 10% hydrochloric acid to dissolve the aluminum salts. The product was extracted with methylene chloride, and the extract was dried over sodium sulfate and concentrated. The crystalline residue was sublimed at 0.15 mm. with a heating block temperature of 170°, and yielded 130.5 mg. (87%) of VII, m.p. 178.4–179.8°. In the reductions of VIII with zinc and either acid or base described by Wawzonek,[4] the glycol formed by an intramolecular pinacol reduction was the product.

1,2,5,6-Dibenz-1,3,5,7-cycloöctatetraene (I). **Preparation from V.**—An 18-cm. section of a 53 × 1.1-cm. Pyrex tube was packed with glass helices, and the tube was mounted vertically in an 18-cm. micro combustion furnace. The top of the tube was fitted with a smaller tube constricted at the lower end which contained a glass rod that could be raised and lowered in order to admit the solid diacetate V gradually into the hot tube. A side-tube sealed near the top of the 53-cm. tube was used to admit nitrogen, and the lower end of the tube was attached to a receiver. The tube was heated to 500° (external temperature measured by a thermocouple), nitrogen was introduced slowly, and 4.0 g. of the diacetate V was added gradually through the constricted tube during a period of 25 minutes. A straw-colored liquid which solidified on standing was collected in the receiver. Water containing sufficient sodium hydroxide to neutralize the acetic acid which was formed was added, and the crystalline product was extracted with methylene chloride. The extract was concentrated, and the solid residue was sublimed at 0.2 mm. with a heating block temperature of 130°. Recrystallization of the sublimate from 95% ethanol yielded 1.78 g. (70%) of I, m.p. 106.2–106.9°, which did not depress the melting point of a sample (described below) that was prepared by the method of Fieser and Pechet.[1]

A solution of 99.8 mg. of I in 25 ml. of 95% ethanol was reduced in the presence of 50 mg. of 10% palladium-on-carbon at 25° and atmospheric pressure. After 30 minutes 98% of two molar equivalents of hydrogen had been absorbed, and the reduction stopped. The catalyst was separated, the filtrate was concentrated, and the product was isolated by sublimation at 0.1 mm. with a heating block temperature of 120°. The sublimate of II weighed 79.3 mg. (79%), and melted at 108.5–109°. Recrystallization from 95% ethanol gave pure II, melting point and mixed melting point with a known sample 109.5–110°. Fieser and Pechet[1] describe the reduction of I to II in the presence of Adams platinum catalyst in ethanol at a hydrogen pressure of 2300 p.s.i. during a period of five hours.

1,2,5,6-Dibenz-1,3,5,7-cycloöctatetraene (I). **Synthesis of Fieser and Pechet.**—***o*-Phthalaldehyde** was prepared

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(8) *Organic Syntheses*, **29**, 24 (1949).

(9) H. V. Frost, *Ann.*, **250**, 156 (1888).

(10) A. Lapworth and J. A. McRae, *J. Chem. Soc.*, **121**, 1709 (1922).

(11) K. Brand and O. Loehr, *J. prakt. Chem.*, **109**, 359 (1925).

(12) W. Roser, *Ann.*, **247**, 152 (1888).

(13) K. Brand and K. O. Müller, *Ber.*, **55**, 601 (1922).

from α,α,α′,α′-tetrabromo-o-xylene by the method of Thiele and Günther[14] except that 800 g. of disodium phosphate ($Na_2HPO_4\cdot 12H_2O$) was added to the reaction mixture before the steam distillation, which required distillation of 24 l. of water. The o-phthalaldehyde obtained from 400 g. of the tetrabromide after crystallization from petroleum ether weighed 104 g. (82%) and melted at 54.5–55.5°.

o-Phenylenediacetonitrile was prepared by a modification of the procedure of Moore and Thorpe.[15] α,α′-Dibromo-o-xylene (66.5 g.) was added to a solution of 35 g. of potassium cyanide in 150 ml. of water and 150 ml. of 95% ethanol at a rate which maintained the reflux temperature. The solution was heated under reflux for two hours, diluted with 500 ml. of water, and the black oil which separated was extracted with four 100-ml. portions of ether. The combined extracts were dried over sodium sulfate, concentrated, and the residue was purified by a short-path distillation at 0.15 mm. The distillate was condensed at a temperature above 18° to avoid explosions during its crystallization.[15] The brown solid product, m.p. 58–59°, on crystallization from 95% ethanol yielded 26.9 g. (68%) of colorless o-phenylenediacetonitrile, m.p. 58–59°.

3,8-Dicyano-1,2,5,6-dibenz-1,3,5,7-cycloöctatetraene was prepared by the procedure of Fieser and Pechet[1] from 3.0 g. of o-phthaldehyde and 3.0 g. of o-phenylenediacetonitrile in a yield of 2.35 g. (48%), m.p. 217.3–217.6°.

Diethyl 1,2,5,6-dibenz-1,3,5,7-cycloöctatetraene-3,8-dicarboxylate was prepared by alcoholysis of the dinitrile,[1] but it was necessary to add water to the reaction mixture or the dinitrile was recovered unchanged. Dry hydrogen chloride was passed through a solution of 1.0 g. of 3,8-dicyano-1,2,5,6-dibenz-1,3,5,7-cycloöctatetraene in 50 ml. of absolute ethanol and 0.1 ml. of water until the solution became warm, after which the gas flow was diminished to about five bubbles per minute and the solution was heated under reflux for eight hours. The mixture was filtered to separate ammonium chloride, the filtrate was concentrated under reduced pressure, and 100 ml. of ether and 100 ml. of water were added to the crystalline residue. The ether layer was separated, washed with 10% aqueous sodium carbonate and water, and concentrated. The residue crystallized, and recrystallization from 95% ethanol yielded 1.1 g. (80%) of diethyl 1,2,5,6-dibenz-1,3,5,7-cycloöctatetraene-3,8-dicarboxylate, m.p. 117.5–118.5°.

1,2,5,6-Dibenz-1,3,5,7-cycloöctatetraene-3,8-dicarboxylic acid was prepared from 0.95 g. of the diethyl ester by the procedure of Fieser and Pechet[1] in a yield of 0.70 g. (88%), m.p. 290–291°.

1,2,5,6-Dibenz-1,3,5,7-cycloöctatetraene (I) was prepared by decarboxylation of the dicarboxylic acid by a modification of the procedure described previously.[1] 1,2,5,6-Dibenz-1,3,5,7-cycloöctatetraene-3,8-dicarboxylic acid (0.500 g.) and 40 g. of copper powder were mixed thoroughly in a mortar. The mixture was placed in a sublimation tube, covered with 3 g. of copper powder, and heated to 270° at a pressure of 30 mm. The yellow distillate crystallized rapidly. The combined distillates from twelve such decarboxylations were sublimed at 0.3 mm. with a heating block temperature of 125°, and yielded 1.73 g. (41%) of crude I. Recrystallization from 95% ethanol yielded 1.39 g. (33%) of pure I melting at 106.5–107°.

A sample of I prepared by this route was characterized by ozonization. A solution of 200 mg. of I in 25 ml. of ethyl acetate was treated with a stream of ozone and oxygen delivering 10 mg. of ozone per minute for 15 minutes at 0°. Glacial acetic acid (15 ml.) and 5 ml. of 35% hydrogen peroxide were added, and the mixture was heated under reflux for 12 hours. The solvent was distilled under reduced pressure, and the crystalline residue was dissolved in 5% aqueous sodium bicarbonate. The solution was acidified with hydrochloric acid and extracted with ether. The extracts were concentrated and the residue was sublimed at atmospheric pressure, yielding 248.2 mg. (86%) of phthalic anhydride, melting point and mixed melting point with an authentic sample 129.5–130.5°.

CAMBRIDGE, MASSACHUSETTS RECEIVED AUGUST 31, 1950

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[14] J. Thiele and O. Günther, *Ann.*, **347**, 107 (1906).

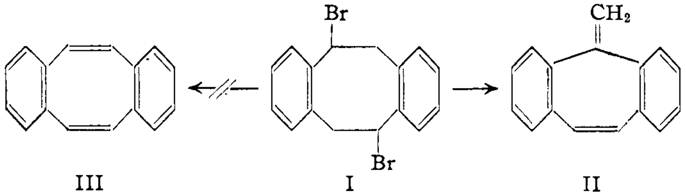
[15] C. W. Moore and J. F. Thorpe, *J. Chem. Soc.*, **93**, 175 (1908).

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

Cyclic Polyolefins. XV. 1-Methylene-2,3,6,7-dibenzcycloheptatriene

BY ARTHUR C. COPE AND STUART W. FENTON

The dehydrobromination of 3,7-dibromo-1,2,5,6-dibenz-1,5-cycloöctadiene (I) by reaction with amines results in molecular rearrangement and the formation of 1-methylene-2,3,6,7-dibenzcycloheptatriene (II) instead of the expected *sym*-dibenzcycloöctatetraene (III). The structure of II was established by oxidation, hydrogenation to 1-methyl-2,3,6,7-dibenzcycloheptadiene (IV), and by independent syntheses of II and IV.



III I II

The synthesis and proof of structure of 3,7-dibromo-1,2,5,6-dibenz-1,5-cycloöctadiene (I) were described in the preceding paper.[1] This paper reports an unusual case of rearrangement resulting in ring contraction which occurred when the dibromide I was treated with bases, including dimethylamine, diethylaniline, 2,6-lutidine, triethylamine, quinoline and α-picoline. Dehydrobromination occurred in each case, forming a colorless, crystalline hydrocarbon (II), $C_{16}H_{12}$, melting at 120°. The highest yields of II (70%) were obtained from I by treatment with α-picoline at the reflux temperature for approximately seven days. The hydrocarbon II proved to be an isomer of the expected dehydrobromination product, *sym*-dibenzcycloöctatetraene[1,2] (III), which melts at 107°.

The dehydrobromination product II gave unsaturation tests with bromine and potassium permanganate, dissolved in concentrated sulfuric acid to give a brilliant red solution that became colorless on addition of water, and absorbed two molar equivalents of hydrogen in a quantitative reduction in the presence of a palladium catalyst. The reduction product obtained from II was not the crystalline *sym*-dibenzcycloöctadiene,[1,3] but a liquid

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[1] A. C. Cope and S. W. Fenton, THIS JOURNAL, **73**, 1668 (1951).

[2] L. F. Fieser and M. M. Pechet, *ibid.*, **68**, 2577 (1946).

[3] W. Baker, R. Banks, D. R. Lyon and F. G. Mann, *J. Chem. Soc.*, 27 (1945).