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).

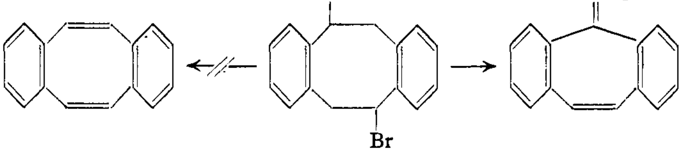
[15] C. W. Moore and J. F. Thorpe, *J. Chem. Soc.*, **93**, 175 (1908).

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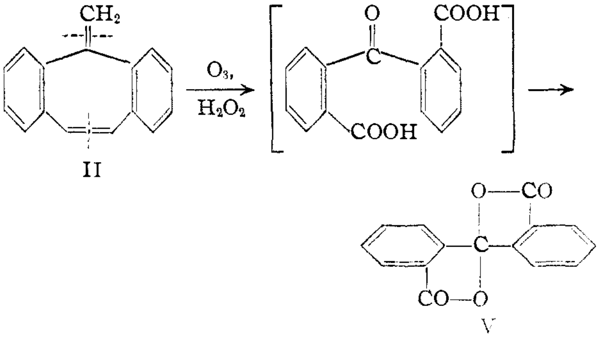
[1] A. C. Cope and S. W. Fenton, THIS JOURNAL, **73**, 1668 (1951).

[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).

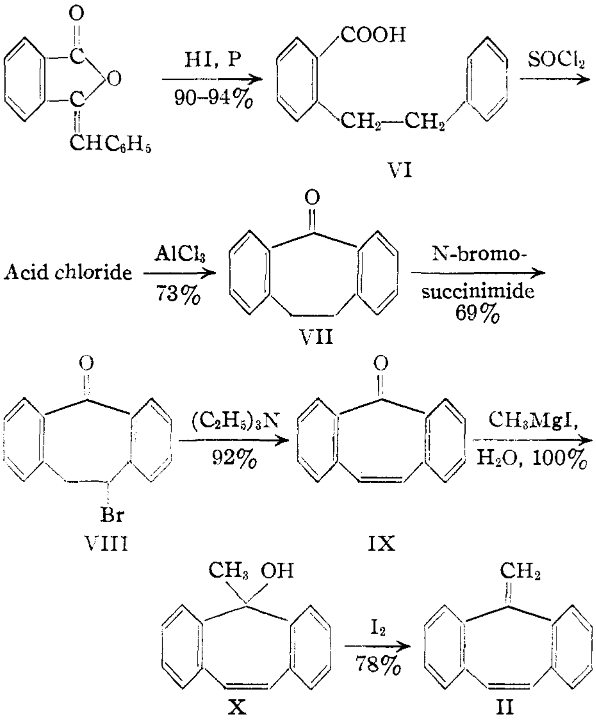
hydrocarbon $C_{16}H_{16}$, which later was proved to be 1-methyl-2,3,6,7-dibenzcycloheptadiene (IV).

Evidence for the structure of II was obtained by ozonization. Treatment with an excess of ozone followed by decomposition of the ozonide with hydrogen peroxide in acetic acid gave misleading information, for the product (isolated by sublimation) was phthalic anhydride, which is formed by the degradation of III under these conditions.[1] However, the yield of phthalic anhydride never exceeded 44% of the two molar equivalents expected from III. Ozonization of II with a slight excess of ozone followed by decomposition of the ozonide with hydrogen peroxide and subsequent sublimation formed the lactone of benzophenone-2,2'-dicarboxylic acid (V)[4] in 69.5% yield, and accordingly provided evidence that the hydrocarbon has structure II. The identity of the lactone V was established by direct comparison with a known sample.



Conclusive proof of the structure of the hydrocarbon II was obtained by independent syntheses of II and its hydrogenation product, IV. These syntheses began with benzalphthalide, which was reduced to 2-(2-phenylethyl)-benzoic acid (VI) in 90–94% yield with phosphorus and hydriodic acid by a modified procedure based on one described by Schlenk and Bergmann.[5] The acid chloride was prepared from VI and thionyl chloride, and without isolation was cyclized to 2,3,6,7-dibenz-2,6-cycloheptadiene-1-one (VII) by treatment with aluminum chloride in carbon disulfide. The yield of VII was very small when slightly more than one molar equivalent of aluminum chloride was used, but was increased to 73% by employment of a large excess. Bromination of VII with N-bromosuccinimide in carbon tetrachloride formed a small amount of a dibromo compound and 4-bromo-2,3,6,7-dibenz-2,6-cycloheptadiene-1-one (VIII) in 69% yield. A short path distillation of VIII at 0.15 mm. resulted in nearly complete dehydrobromination, and the crude product when treated with triethylamine formed 2,3,6,7-dibenz-2,4,6-cycloheptatriene-1-one (IX) in 92% yield from VIII. The over-all yield of IX from VII was 61.4% if VIII was not isolated.

Evidence that no rearrangement had occurred in the dehydrobromination of VIII (which might have led to the formation of 9-methyleneanthrone instead of IX) was obtained by ozonization of IX followed by oxidation of the ozonide with hydrogen peroxide and sublimation of the product, which formed the lactone of benzophenone-2,2'-dicarboxylic acid (V) in 71% yield. The addition of methylmagnesium iodide to IX followed by hydrolysis formed 1-methyl-2,3,6,7-dibenz-2,4,6-cycloheptatriene-1-ol (X) in essentially quantitative yield, and dehydration of the tertiary alcohol X by heating under reduced pressure, preferably after addition of a small amount of iodine, furnished an authentic sample of 1-methylene-2,3,6,7-dibenz-2,4,6-cycloheptatriene (II) in 78% yield. This sample of II was proved to be identical with the product formed by dehydrobromination of I by comparison of melting points, mixed melting point and infrared spectra (Fig. 1).



Reduction of the authentic sample of II yielded 1-methyl-2,3,6,7-dibenz-2,6-cycloheptadiene (IV). A separate synthesis of IV also was undertaken which did not involve a dehydrobromination step, in order to establish the structure of the carbon skeleton beyond any doubt. The ketone 2,3,6,7-dibenz-2,6-cycloheptadiene-1-one (VII), prepared by the route described above, was treated with methylmagnesium iodide. Hydrolysis gave a nearly quantitative yield of 1-methyl-2,3,6,7-dibenz-2,6-cycloheptadiene-1-ol (XI), which was very easily dehydrated. Sublimation of XI under reduced pressure after addition of a trace of iodine formed 1-methylene-2,3,6,7-dibenz-2,6-cycloheptadiene (XII)[5a] in 99% yield as a colorless, crystalline solid, m. p. 63–64°. Hydrogenation of XII in the presence of a palladium catalyst resulted in the absorption of one molar equivalent of hydrogen, and formed an authentic sample of 1-methyl-2,3,6,7-dibenz-2,6-cycloheptadiene (IV), with essentially the same boiling point, index of re-

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(4) C. Graebe and P. Juillard, *Ann.*, **242**, 246 (1887).

(5) W. Schlenk and E. Bergmann, *ibid.*, **463**, 267 (1928).

(5a) NOTE ADDED IN PROOF: Since this work was completed W. Treibs and H. Klinkhammer, *Chem. Ber.*, **83**, 367 (1950), have described the synthesis of XII by the same sequence: VI → VII → XI → XII.

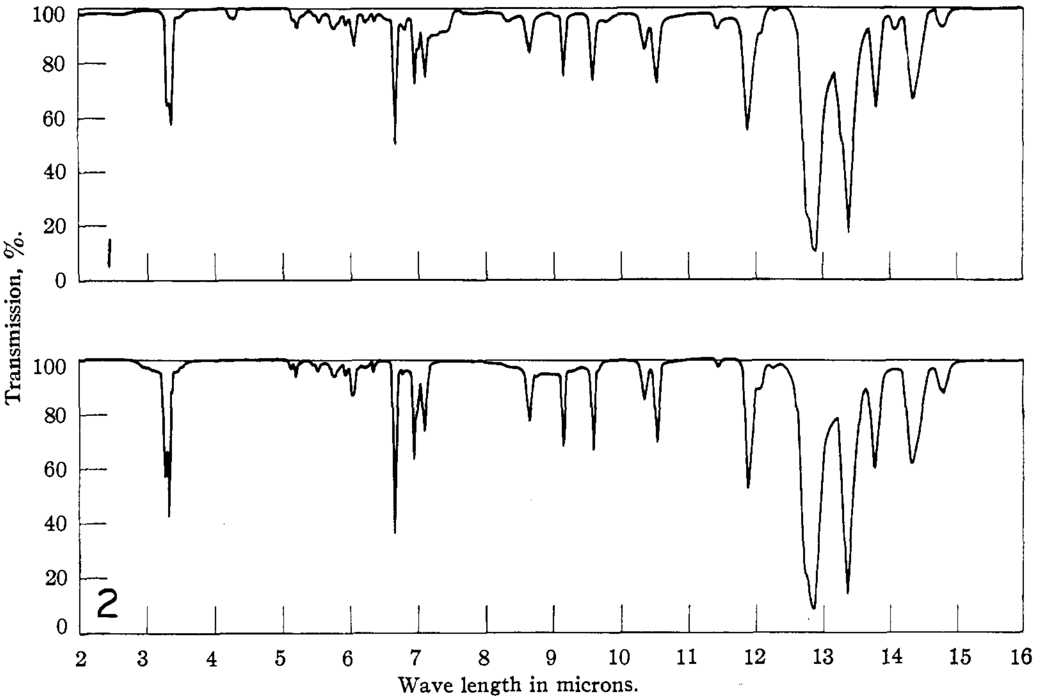
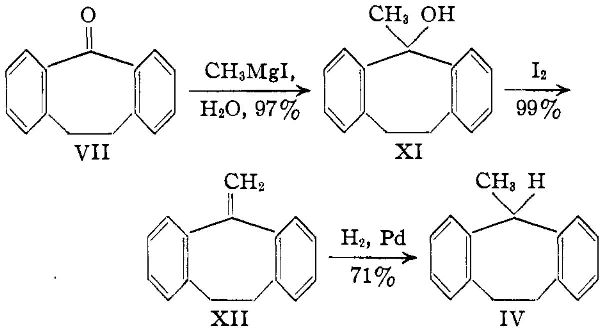


Fig. 1.—Infrared absorption spectrum of 1-methylene-2,3,6,7-dibenzcycloheptatriene (II): curve 1, sample prepared from I by dehydrobromination; curve 2, sample prepared from X. The spectra were determined for 10% solutions in carbon tetrachloride in the region 2–12 μ and for 10% solutions in carbon disulfide in the region 12–16 μ.

fraction and infrared spectrum (Fig. 2) as a sample of IV obtained by reduction of II (prepared by the dehydrobromination of I).



The evidence obtained for the structure of II by ozonization, hydrogenation, and independent syntheses of II and its hydrogenation product IV makes it certain that the dehydrobromination of I occurs with molecular rearrangement and conversion of the eight-membered ring of I to the seven-membered ring of II. This rearrangement might occur in either the first or the second dehydrobromination step, or might result from initial formation of the eight-membered *sym*-dibenzcycloöctatetraene (III) followed by rearrangement of III to II. Evidence that the last explanation is incorrect was obtained from the observation that III was recovered unchanged after heating with a solution of α-picoline hydrobromide in α-picoline under the conditions which result in conversion of I to II. The ring system of III when once formed is quite stable, for no rearrangement occurred when III was heated with hydrogen bromide and benzoyl peroxide, or heated with iodine during irradiation by ultraviolet light. The ring system of 1,2,5,6-dibenz-1,5-cycloöctadiene also is stable, for that hydrocarbon was recovered unchanged after heating with α-picoline hydrobromide in α-picoline, or heating with the strong bases, potassium *t*-butoxide and *n*-butyllithium.

Further study of the dehydrobromination of compounds related to II is planned in order to determine the step at which molecular rearrangement occurs.

Experimental[6]

1-Methylene-2,3,6,7-dibenz-2,4,6-cycloheptatriene (II). —A solution of 5.0 g. of 3,7-dibromo-1,2,5,6-dibenz-1,5-cycloöctadiene[1] (I) in 100 ml. of α-picoline was heated under reflux in a nitrogen atmosphere for 7 days. Most of the α-picoline (80 ml.) was separated by distillation at atmospheric pressure, and the residue was cooled and acidified with dilute phosphoric acid. An oil which crystallized rapidly separated, and was extracted with methylene chloride. After distillation of the solvent the residue was sublimed in a short-path still at 0.1 mm. and a heating block temperature of 125°. The crystalline distillate was recrystallized from 95% ethanol as colorless plates (1.94 g., 70%) melting at 118.4–119.4°. An analytical sample prepared by resublimation and recrystallization from 95% ethanol melted at 119.7–120.3°, and no depression was observed in a mixed melting point with an authentic sample of II described below (m.p. 119.8–120.4°).

Anal. Calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 94.17; H, 6.04.

When solutions of I in triethylamine, diethylaniline or 2,6-lutidine were heated under reflux for prolonged periods, dehydrobromination and rearrangement occurred, but the yields of II were lower than those obtained using α-picoline. Quinoline at 125–150° converted I to II in yields comparable to those obtained with α-picoline, but at higher temperature

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[6] Melting points are corrected and boiling points are uncorrected. We are indebted to Mr. S. M. Nagy and his associates for analyses and for infrared spectra, which were determined with a Baird Double Beam Infrared Recording Spectrometer, Model B, fitted with a sodium chloride prism.

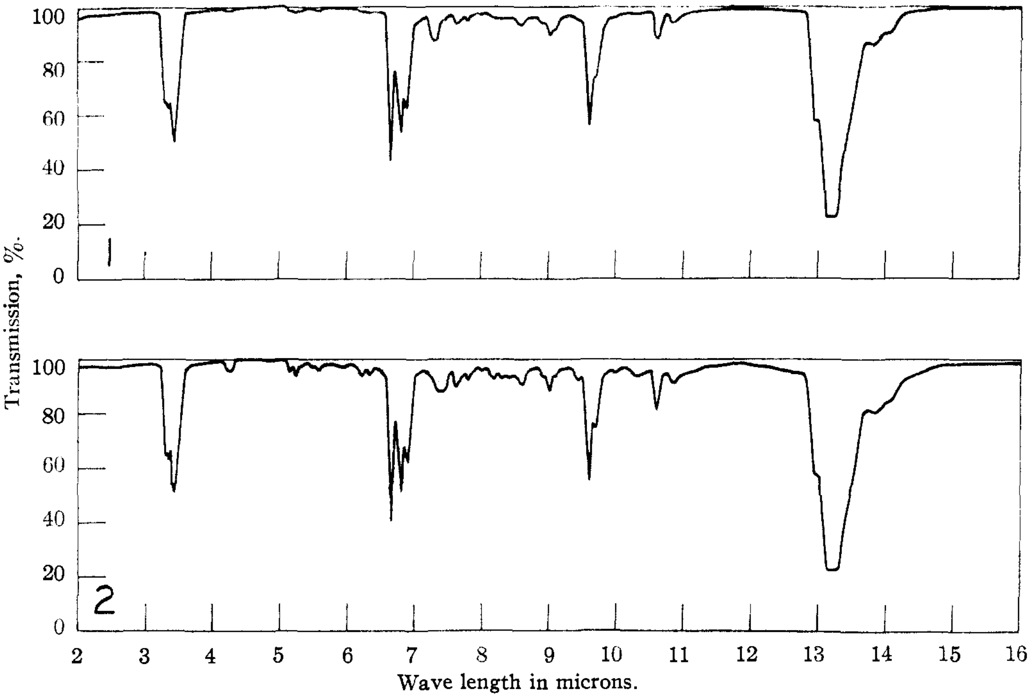

Fig. 2.—Infrared absorption spectrum of 1-methyl-2,3,6,7-dibenz-2,6-cycloheptadiene (IV): curve 1, sample prepared by hydrogenation of XII; curve 2, sample prepared by hydrogenation of II (obtained from I). The spectra were determined for 10% solutions in carbon tetrachloride in the region 2–12 μ and for 10% solutions in carbon disulfide in the region 12–16 μ.

decomposition occurred resulting in the formation of a red amorphous solid.

1-Methyl-2,3,6,7-dibenz-2,6-cycloheptadiene (IV).—Hydrogenation of 2.00 g. of II in 75 ml. of 95% ethanol in the presence of 0.1 g. of 10% palladium-on-carbon[7] at atmospheric pressure and room temperature was complete in 2 hours, and required 96.5% of two molar equivalents of hydrogen. The catalyst was separated by filtration, and the product was distilled in a short path still at 0.5 mm. with a heating block temperature of 130°. Redistillation through a semi-micro column[8] yielded 1.69 g. (83%) of IV as a colorless liquid, b.p. 118–118.5° (0.45 mm.), $n^{25}\text{D}$ 1.6045, d^{25}_4 1.0789. These properties are very similar to the properties of a known sample of IV described below.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.52; H, 7.75.

The reduction of II to IV also occurred when a solution of II in a mixture of dry ether and liquid ammonia was treated with an excess of sodium. After addition of ammonium chloride IV was separated by extraction and isolated by distillation in 72% yield.

Ozonization of II.—A solution of 200 mg. of II in 25 ml. of ethyl acetate was cooled to −70°, and treated at that temperature with a stream of oxygen and ozone furnishing 10 mg. of ozone per minute for 11 minutes. A solution of 5 ml. of 35% hydrogen peroxide in 20 ml. of glacial acetic acid was added, and the resulting solution was heated under reflux for 4 hours and then concentrated under reduced pressure. A solution of the residue in excess 10% aqueous sodium bicarbonate was acidified with hydrochloric acid, and the acids formed were extracted with ether. The extracts were concentrated, and the residue was sublimed at 0.2 mm. The more volatile product was 19.3 mg. of phthalic anhydride, m.p. 129–130°. The lactone of benzophenone-2,2′-dicarboxylic acid[4] (V) was collected as a less volatile fraction (171.9 mg., 69.5%), which after recrystallization from 95% ethanol amounted to 105.5 mg. and melted at 208–211°. The sample of V formed in this manner was characterized by analysis and by a mixed melting point with a sample prepared from IX (described below), which showed no depression.

Treatment of a solution of 200 mg. of II in 25 ml. of ethyl acetate with a stream of oxygen furnishing 10 mg. of ozone per minute for 35 minutes at room temperature, followed by decomposition of the ozonide with hydrogen peroxide and acetic acid and sublimation of the product yielded 122 mg. of phthalic anhydride (83% yield based on structure II or 42% based on structure III).

Synthesis of II. 2-(Phenylethyl)-benzoic Acid (VI).—Benzalphthalide[9] (40 g.), 15 g. of red phosphorus and 200 ml. of 57% hydriodic acid were heated under reflux for 6 hours. An additional 10-g. portion of red phosphorus was added and refluxing was continued for a period of 6 hours. The reaction mixture was cooled and poured onto 500 g. of ice with stirring. The red insoluble solid was separated by filtration and heated under reflux with 100 ml. of 28% ammonium hydroxide for 20 minutes. The mixture was filtered, and the colorless filtrate was acidified with dilute hydrochloric acid. The colorless solid product weighed 40 g. (99%) after drying, and melted at 128–130°. Recrystallization from 70% ethanol yielded 38.2 g. (94%) of VI, m.p. 129–130°. This procedure differs from the one described by Schlenk and Bergmann,[5] who obtained a 36% yield, in the use of a smaller amount of phosphorus and a longer reaction period.

2,3,6,7-Dibenz-2,6-cycloheptadiene-1-one (VII).—A mixture of 44.2 g. of the acid VI and 100 ml. of thionyl chloride was heated on a steam-bath under reflux until gas evolution ceased. The excess thionyl chloride was removed by distillation under reduced pressure, and 800 ml. of carbon disulfide and 40 g. of aluminum chloride were added to the residual oil. The mixture was allowed to stand at room temperature for 18 hours, after which it was cooled and cracked ice was added slowly. The carbon disulfide was removed by distillation and the product was extracted from the resulting aqueous suspension with two 100-ml. portions of ether. The ether extracts were washed with 10% sodium hydroxide solution and water, dried over magnesium sulfate, and concentrated. Distillation of the residue yielded 30.3 g. (73%) of VII, b.p. 148° (0.3 mm.). A sample obtained from a similar preparation was analyzed; b.p. 133–134° (0.15 mm.), $n^{25}\text{D}$ 1.6332, d^{25}_4 1.1613.

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(7) *Org. Syntheses*, **26**, 32 (1946).

(8) C. W. Gould, G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

(9) "Organic Syntheses," Coll. Vol. 2, John Wiley & Sons, Inc., New York, N. Y., 1943, p. 61.

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.50; H, 5.81. Found: C, 86.53; H, 5.82.

4-Bromo-2,3,6,7-dibenz-2,6-cycloheptadiene-1-one (VIII).—A mixture of 4.95 g. of N-bromosuccinimide, 5.1 g. of VII and 50 ml. of carbon tetrachloride was heated under reflux for 3 hours. The mixture was cooled, filtered to separate succinimide, and the filtrate was washed with water. After distillation of part of the solvent under reduced pressure a light yellow, crystalline dibromide separated (1.30 g.). The dibromide melted at 200–207° (dec.). It was quite insoluble in ordinary solvents and not very stable, and was not purified. An analysis of the crude dibromide was in fair agreement with the formula $C_{15}H_{10}Br_2O$. Removal of the remainder of the solvent left a yellow crystalline residue of crude VIII (4.86 g., 69%), m.p. 77–84° (dec.). An analytical sample was recrystallized from ligroin as a pale yellow solid, m.p. 85.6–87.6° (dec.).

Anal. Calcd. for $C_{15}H_{11}BrO$: C, 62.74; H, 3.86. Found: C, 62.65; H, 4.17.

2,3,6,7-Dibenz-2,4,6-cycloheptatriene-1-one (IX).—A mixture of 10.4 g. of VII, 9.0 g. of N-bromosuccinimide, 0.1 g. of benzoyl peroxide and 100 ml. of carbon tetrachloride was heated under reflux for 1 hour. The succinimide was separated by filtration, and the filtrate was washed with 5% sodium hydroxide and water. The crystalline residue obtained by distillation of the solvent was heated under reflux with 100 ml. of triethylamine for 2 hours. Triethylamine hydrobromide was formed very rapidly. The mixture was concentrated under reduced pressure, and dilute hydrochloric acid was added to the residue. The crystalline solid which separated was purified by a short path distillation at 0.3 mm. with a heating block temperature of 200°. The product contained a small amount of bromine, and was again treated with 100 ml. of triethylamine for 6 hours at the reflux temperature. After separation of the triethylamine by the procedure described above the product was purified by two crystallizations from 95% ethanol, which yielded 6.4 g. (61%) of IX as colorless needles melting at 88.3–89.2°.

The sublimation of VIII (4.0 g.) at 0.15 mm. and a heating block temperature of 160° also resulted in nearly complete elimination of hydrogen bromide, which was completed by treating the crude product with 25 ml. of triethylamine at the reflux temperature for 3 hours. Purification of the product by recrystallization from 95% ethanol yielded 2.64 g. (92%) of IX, m.p. 87.6–88.5°. An analytical sample recrystallized from 95% ethanol melted at 88.4–89.2°.

Anal. Calcd. for $C_{15}H_{10}O$: C, 87.35; H, 4.89. Found: C, 87.08; H, 5.03.

A solution of 0.20 g. of IX in 25 ml. of ethyl acetate was treated with ozone (10 mg. per minute) at −70° for 5.5 minutes. Glacial acetic acid (20 ml.) and 0.5 ml. of 35% hydrogen peroxide were added, and the solution was heated under reflux for 2 hours. The solvent was removed at 30 mm., and the solid residue was treated with 10% aqueous sodium bicarbonate and extracted with ether to remove a small amount of neutral material. The alkaline solution was acidified with dilute hydrochloric acid, extracted with ether, and the extracts were dried over magnesium sulfate and concentrated. Sublimation of the crystalline residue at 0.3 mm. with a heating block temperature of 120–180° separated 20 mg. of phthalic anhydride, m.p. 128–129.5°, and 174.4 mg. of the lactone of benzophenone-2,2′-dicarboxylic acid (V), m.p. 205–209°. Recrystallization of V from 95% ethanol furnished a pure sample melting at 208–211° with a saponification equivalent of 125.8 (calcd. 126.1).

1-Methyl-2,3,6,7-dibenz-2,4,6-cycloheptatriene-1-ol (X).—Methylmagnesium iodide was prepared under anhydrous conditions from 0.24 g. of magnesium and 1.5 g. of methyl iodide in 50 ml. of dry ether. A solution of 1.0 g. of IX in 25 ml. of dry ether was added dropwise with stirring. A bright yellow solid which redissolved separated initially, and a colorless solid separated at the end of the addition (30 minutes). After stirring the mixture for an additional period of 30 minutes the flask was cooled in ice, and 50 ml. of saturated aqueous ammonium chloride was added slowly. The ethereal layer was separated, washed with water and dried over magnesium sulfate. A colorless crystalline product (1.08 g., 100%), m.p. 110–115° (dec.), was obtained by removing the ether under reduced pressure. An analytical sample of X prepared by three crystallizations from 70% ethanol melted at 112–115° (dec.).

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.24; H, 6.49.

1-Methylene-2,3,6,7-dibenz-2,4,6-cycloheptatriene (II).—The tertiary alcohol X (1.00 g.) was heated in a sublimation tube at 30 mm. with a small crystal at iodine. Dehydration occurred at 100°, and when gas evolution stopped the product was sublimed at 0.15 mm. with a heating block temperature at 140°. Recrystallization of the colorless crystalline product from 95% ethanol yielded 0.72 g. (78%) of II as colorless plates melting at 119.8–120.4°.

Anal. Calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 94.06; H, 6.23.

A solution of 2.0 g. of II (prepared from X) in 75 ml. of 95% ethanol was hydrogenated at atmospheric pressure and room temperature in the presence of 0.2 g. of 10% palladium-on-carbon. The yield of IV, isolated by the procedure described above, was 1.75 g., b.p. 109–110° (0.1 mm.), $n^{25}D$ 1.6027.

1-Methyl-2,3,6,7-dibenz-2,6-cycloheptadiene-1-ol (XI).—Methylmagnesium iodide was prepared under anhydrous conditions from 3.0 g. of methyl iodide and 0.48 g. of magnesium in 30 ml. of dry ether. A solution of 2.00 g. of VII in 20 ml. of dry ether was added dropwise in a period of 30 minutes. A bright red color which appeared initially disappeared when the addition was complete. The reaction mixture was cooled with ice and salt, and 50 ml. of saturated aqueous ammonium chloride was added slowly. The product was isolated in the same manner as X, and was a pale yellow solid (2.1 g., 97%), m.p. 125–140° (dec.). An analytical sample which was recrystallized from 95% ethanol melted at 125–140° (dec.), or if introduced into the melting point-bath at 120° began to decompose at 130° and melted at 135–143.5° (dec.).

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 85.63; H, 7.10.

1-Methylene-2,3,6,7-dibenz-2,6-cycloheptadiene (XII).—The tertiary alcohol XI (1.4 g.) and a small crystal of iodine were placed in a sublimation tube and warmed at a pressure of 30 mm. The distillation of water formed by dehydration began at 80°, and after completion of the reaction the residue was sublimed at 0.25 mm. and a heating block temperature of 120°. The olefin XII collected as colorless crystals melting at 63–64° in a yield of 1.28 g. (99%). An analytical sample which was recrystallized from 95% ethanol melted at 63.5–64°.

Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.19; H, 7.07.

1-Methyl-2,3,6,7-dibenz-2,6-cycloheptadiene (IV).—A solution of 3.00 g. of XII in 100 ml. of 95% ethanol was reduced at 25° and atmospheric pressure in the presence of 0.1 g. of 10% palladium-on-carbon,[7] and absorbed 101% of one molar equivalent of hydrogen in 2 hours. The catalyst was separated by filtration, and the oil obtained by concentrating the filtrate was distilled through a semimicro column. The yield of IV was 2.17 g. (74%), b.p. 108–112° (0.09–0.13 mm.), $n^{25}D$ 1.6022, d^{25}_4 1.0789.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.10; H, 7.69.

Attempted Isomerization of 1,2,5,6-Dibenz-1,5-cyclooctadiene.—1,2,5,6-Dibenz-1,5-cycloöctadiene[1] (1.0 g.) was added to a potassium *t*-butoxide solution prepared from 2.0 g. of potassium and 50 ml. of *t*-butanol, and the solution was heated under reflux for 48 hours. The product was isolated by concentration of the solution, addition of water, extraction with methylene chloride, sublimation and recrystallization from 95% ethanol. It proved to be unchanged 1,2,5,6-dibenz-1,5-cycloöctadiene, m.p. and mixed m.p. with a known sample 109.5–110° (recovery 0.75 g., 75%). Similar results were obtained when 4.12 g. of 1,2,5,6-dibenz-1,5-cycloöctadiene was added to the *n*-butyllithium prepared from 8.5 g. of *n*-butyl bromide and 0.82 g. of lithium, and the solution was heated under reflux for 24 hours. The recovery of 1,2,5,6-dibenz-1,5-cyclooctadiene was 3.52 g. (85.6%). 1,2,5,6-Dibenz-1,5-cycloöctadiene also was recovered to the extent of 82% after a 0.50-g. sample was heated under reflux for 96 hours with 50 ml. of α-picoline containing 2.0 g. of hydrogen bromide.

Attempted Isomerization of 1,2,5,6-Dibenz-1,3,5,7-cyclooctatetraene (III).—A solution of 0.10 g. of III and 0.1 g. of benzoyl peroxide in 50 ml. of dry benzene previously saturated with hydrogen bromide at room temperature was heated under reflux for 12 hours. The solution was extracted with 10% aqueous sodium carbonate, concentrated, and the residue was sublimed under reduced pressure. Recrystallization of the sublimate from 95% ethanol yielded 64.7 mg. (64.7%) of unchanged III, m.p. 105.5–106°. A solution of 0.10 g. of III and 0.1 g. of iodine in 50 ml. of benzene was heated under reflux for 10 hours, illuminated with a 275 watt General Electric sun lamp at a distance of 10 cm. The iodine was removed by extraction with aqueous sodium bisulfite, and 78.2 mg. (78.2%) of III was recovered from the benzene solution by concentration and sublimation at 0.17 mm. with a heating block temperature of 120°. Similar results were obtained by heating 0.20 g. of III and a solution of 1.0 g. of hydrogen bromide in 50 ml. of α-picoline under reflux for 144 hours. The recovery of unchanged III was 169 mg. (84.5%).

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Structural Aspects of the Color Reaction of Lignin with Phenols[1]

BY JOHN C. PEW

The chemistry of the long-known color reaction of lignin with phenols has been investigated. The absorption spectra of the color resulting from the action of resorcinol on spruce "native" lignin in acid solution was found to have a maximum at identical wave length to that of the color resulting from the acidification of catalytically reduced 4′,7-dihydroxy-3′-methoxyflavanone. This is also identical to the maxima obtained by reduction of 2′,4,4′-trihydroxy-3-methoxychalcone with lithium aluminum hydride or by the condensation of coniferylaldehyde with resorcinol in acid solution. With aspen "native" lignin the maximum absorption is between that of reduced 4′,7-dihydroxy-3′-methoxyflavanone and reduced 4′,7-dihydroxy-3′,5′-dimethoxyflavanone. With spruce and aspen wood the resorcinol color corresponds to the condensation product of resorcinol with coniferylaldehyde substituted in the 5 position with a methoxyl or propenyl group.

Although the color reactions of lignin with phenols have been known a long time[3,4] and the literature on the subject is rather extensive, the chemistry involved has not been clearly established. The phenol reagent most used as a color test for lignin has been phloroglucinol and hydrochloric acid (Wiesner reagent). Much confusion has resulted from claims that numerous substances (coniferin, vanillin, ferulic acid, aliphatic aldehydes, clove oil, sassafras oil, cinnamaldehyde, piperonal, salicylaldehyde, hydroxyfurfural, eugenol, glucoseen, etc.) give a "lignin reaction" with this solution. Actually, in many cases the colors produced are not even visually similar to that obtained with lignin; in other instances, impurities in the compounds are responsible. Thus it is easily demonstrated that vanillin gives an orange color with the phloroglucinol reagent rather than the purple-red color produced by wood. Klason[5] has shown that coniferin and coniferyl alcohol, when purified, no longer give the color and Herzog and Hillmer[6] indicated that isoeugenol gives a positive reaction only after auto-oxidation. Recently Adler, Björkqvist and Häggroth[7] showed that eugenol, which gives color reactions with phenols that are very similar to those obtained with lignin, contains coniferyl aldehyde and its methyl ether, which are responsible for the reaction, and also confirmed the fact that pure coniferyl alcohol is without action.

A further complication arises in the claim[8,9] that the color reactions are not due to the lignin, but rather to "traces of materials of aldehydic nature which always accompany lignin." Brauns,[10] however, concluded that the phloroglucinol color reaction is a fundamental property of spruce wood and this view appears to be currently accepted.

In spite of the rather extensive work on the subject, few investigators have even hazarded a guess as to the chemical structure of the chromophoric group developed. Hagglund and Johnson[11] claimed that a free hydroxyl group must be present in the phenol used and that a semi-acetal is produced. References to aldehydic groups and coniferylaldehyde as the causative agents are, however, fairly numerous.

Although the groups in lignin responsible for this color reaction probably form only a small part of the molecule (Adler and Ellmer[12] estimate one group to between 40 and 60 phenylpropane units), it was hoped that the placing of the reaction on a structural basis might give information on linkages within the main portion of the compound. A means of attacking the problem of structure was found some years ago in the observation that the reduction of properly substituted flavanones gave colors strikingly similar to those produced by wood with the appropriate phenol. Investigation of the literature at that time revealed that, although the flavanones were well established in structure, the chemistry of their reduction products was in an unsatisfactory state. The work of Geissman and Clinton[13] clarified this matter.

Results

Brauns' spruce "native" lignin was chosen as the first substance to investigate, since it is soluble in alcohol, gives the color reaction readily, and, if not identical with the bulk of the lignin in wood, probably is very closely allied to it. Figure 1 gives the absorption spectra produced by the re-

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(2) Maintained at Madison, Wis., in coöperation with the University of Wisconsin.

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