trans-**10-Hydroxymethyl-2-*cis*-decalol (IV).**—A solution of 0.38 g. (0.010 mole) of sodium borohydride in 10 cc. of methanol was added in portions to 3.64 g. (0.020 mole) of hydroxymethyldecalone XIII. The reaction mixture stood at room temperature for 6 hours. Treatment with 2.5 cc. of acetic acid and removal of the methanol was followed by the addition of 50 cc. of water and solid potassium carbonate until strongly alkaline. The product was extracted with chloroform and it crystallized from the concentrated chloroform solution upon dilution with hexane; yield 2.4 g. (75%), m.p. 120–123°. Several recrystallizations from chloroform–benzene gave 1.8 g. (50%) of pure diol IV, m.p. 139–140°, depression when mixed with I, II or III.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.3; H, 10.7.

The bis-*p*-nitrobenzoate derivative was prepared in 98% yield in pyridine–ether, m.p. 197–198°. A sample for analysis melted at 198°, from ethanol.

Anal. Calcd. for $C_{25}H_{26}O_8N_2$: C, 62.23; H, 5.43. Found: C, 62.2; H, 5.1.

The impure diol residues from the original chloroform extract and from recrystallization liquors were combined. These amounted to 1.7 g., m.p. 113–124°. Conversion to the bis-*p*-nitrobenzoate derivative gave a mixture not separable by crystallization, m.p. 135–175°. The ether-soluble bis-*p*-nitrobenzoate derivative of III was partly separated from the less soluble derivative of IV by treatment with boiling ether. Several recrystallizations from alcohol furnished small amounts of these materials, m.p. 135–137° and 198°, respectively, no depression when either was mixed with its respective authentic sample.

When 1.00 g. (5.5 millimoles) of 10-hydroxymethyl-2-*cis*-decalone (XIII) in ethanol was shaken with platinum oxide at one atmosphere, there was recovered 0.77 g. (75%) of *trans*-10-hydroxymethyl-2-*cis*-decalol (IV), m.p. 134–137°, from chloroform–hexane.

When 0.200 g. (1.1 millimoles) of the unsaturated ketone XIV was treated in the same way, two volumes of hydrogen were rapidly absorbed. The yield of IV which crystallized from chloroform–hexane was 0.150 g. (74%), m.p. 132–134°, no depression.

10-Hydroxymethyl-2-*trans*-decalone (XV).—10-Hydroxymethyl-2-*trans*-decalone-2-dioxolan was prepared from 2-carbethoxy-2-*trans*-decalone[2,3,7] as described by Dreiding and Tomasewski.[5] The hydrolysis of 5.00 g. (0.022 mole) of this material was effected by 1 hour at reflux in 30 cc. of methanol to which 30 cc. of 5% hydrochloric acid had been added. The product was extracted with ether and washed with sodium bicarbonate. Distillation gave 3.00 g. (75%) of XV, b.p. 124–129° at 0.6 mm., $n^{25}\text{D}$ 1.5145.

A 2,4-dinitrophenylhydrazone derivative melted at 104–106° after recrystallization from ethanol.

Anal. Calcd. for $C_{17}H_{22}O_5N_4$: N, 15.46. Found: N, 15.3.

cis-**10-Hydroxymethyl-2-*trans*-decalol (I).**—A sample of the ketone XV (0.406 g., 2.23 millimoles), was shaken in ethanol over platinum oxide with hydrogen at one atmosphere pressure. When crystallized from chloroform–hexane, 0.202 g. (50%) of *cis*-*trans*-diol I was obtained, m.p. 143–144°, no depression.

The bis-*p*-nitrobenzoate derivative was prepared in 93% yield, m.p. 153–154°. An analytical sample melted at 155–156°, from ethanol.

Anal. Calcd. for $C_{25}H_{26}O_8N_2$: C, 62.23; H, 5.43. Found: C, 61.8; H, 5.3.

EVANSTON, ILLINOIS

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

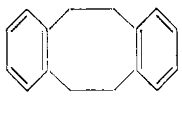
Cyclic Polyolefins. XXXIX. 1,2,3,4-Dibenz-1,3-cycloöctadiene

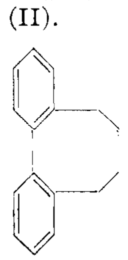
BY ARTHUR C. COPE AND RONALD DEAN SMITH[1]

RECEIVED SEPTEMBER 6, 1955

1,2,3,4-Dibenz-1,3-cycloheptadien-6-one (III) has been converted to the next higher ring-homolog, 1,2,3,4-dibenz-1,3-cycloöctadien-6-one (VIII), by the Tiffeneau–Demjanov method of ring expansion. The aminoalcohol precursor of VIII was synthesized from III by a sequence in which the Reformatsky reaction was used to prepare the hydroxy ester IV, which was converted to the hydrazide V. Reaction of the hydrazide with nitrous acid formed the oxazolidone VI, and subsequent hydrolysis yielded the aminoalcohol VII. The ketone VIII was reduced with sodium borohydride to an alcohol IX, which was dehydrated with boric acid to a mixture of trienes, Xa and Xb. Both hydrogenation of this mixture and Wolff–Kishner reduction of the ketone VIII formed the hydrocarbon, 1,2,3,4-dibenz-1,3-cycloöctadiene (II). The physical properties of this hydrocarbon, in particular its ultraviolet spectrum, are of interest.

The preparation of 1,2,5,6-dibenz-1,5-cycloöctadiene (I)[2,3a,b] and its conversion to *sym*-dibenzcycloöctatetraene[3b] have been described previously. This paper reports the preparation of an isomer of I, 1,2,3,4-dibenz-1,3-cycloöctadiene (II).


I


II

1,2,3,4-Dibenz-1,3-cycloheptadien-6-one (III) was prepared as an intermediate in the synthesis by the method first described by Kenner and Turner,[4] with modifications described in the Experimental section that resulted in an improved yield. Attempted ring expansion of the ketone III by treatment with diazomethane by both the *in situ* and *ex situ* procedures[5] led to complex mixtures that could not be separated readily. The ketone III failed to react with hydrogen cyanide in the presence of piperidine, or with nitromethane in the presence of sodium ethoxide, so these routes to compounds reducible to the aminoalcohol VII could not be used. It was possible to prepare VII by an indirect route, beginning with the Reformatsky reaction of the ketone III with ethyl bromoacetate and zinc, which formed the ethyl ester of 6-hydroxy-1,2,3,4-dibenz-1,3-cycloheptadien-6-acetic acid (IV) in 84% yield. Reaction of this β-hydroxy ester with hydrazine yielded the corresponding hydrazide V (89%). The crude acid azide obtained by treating V with

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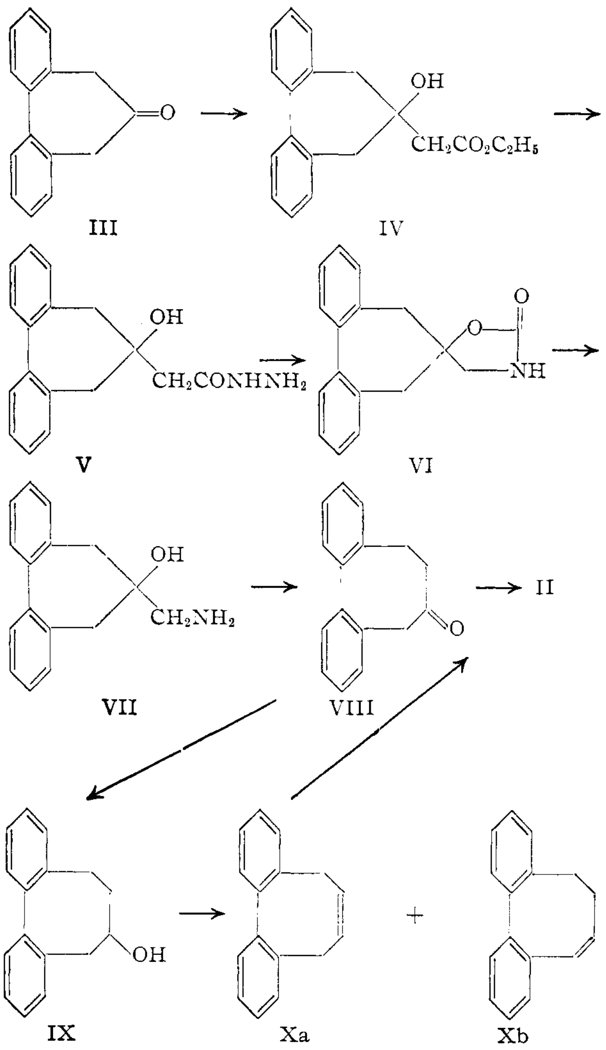
[1] National Science Foundation Fellow, 1953–1955.

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

[3] (a) L. F. Fieser and M. M. Pechet, THIS JOURNAL, **68**, 2577 (1946); (b) A. C. Cope and S. W. Fenton, *ibid.*, **73**, 1688 (1951).

[4] J. Kenner and E. G. Turner, *J. Chem. Soc.*, **99**, 2101 (1911).

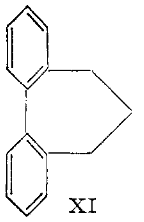
[5] C. D. Gutsche, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, 1954, p. 364.

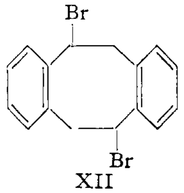


nitrous acid was heated in benzene, and yielded 1-oza-3-aza-7,8,9,10-dibenzspiro[4.6]undeca-7,9-dien-2-one (78%). The transformation of β-hydroxy-acid azides to oxazolidones during the Curtius reaction was first reported by Schroeter[6] and has been employed recently by several other workers.[7-10] It has also been reported that acid hydrolysis and decarboxylation of oxazolidones to give aminoalcohols occurs readily.[6-10] However, the oxazolidone VI was hydrolyzed very slowly by concentrated hydrochloric acid at 100° and by a mixture of concentrated hydrochloric acid and glacial acetic acid at 100°. Basic hydrolysis and decarboxylation occurred much more readily. Treatment of VI with ethanolic potassium hydroxide gave the aminoalcohol VII in a yield of 90%.

The reaction of VII with nitrous acid gave a mixture of ketonic and non-ketonic material which could be separated by the use of Girard reagent.[11] The ketone VIII, which could be isolated easily from the ketonic fraction, was obtained in a yield of 34%. Wolff–Kishner reduction of VIII afforded the hydrocarbon II in a yield of 82%. Reduction of VIII with sodium borohydride gave 1,2,3,4-dibenz-1,3-cycloöctadien-6-ol (IX) in 86% yield. Dehydration of this alcohol by boric acid formed a mixture of isomeric hydrocarbons, Xa and Xb. An attempt to isomerize Xa to Xb by heating the mixture with ethanolic sodium ethoxide was unsuccessful. The mixture of olefins on hydrogenation in the presence of a palladium catalyst gave the hydrocarbon II.

The properties of II are quite different from those of its isomer I. The hydrocarbon II melts at 151°, while I, which appears to be more symmetrical in a planar projection formula, melts at 110°.[1] 1,2,3,4-Dibenz-1,3-cycloheptadiene (XI), a compound similar to II but containing one less methylene group in the non-aromatic ring, exists in dimorphous forms of m.p. 40° and 55°.[12] The solubility of II in ethanol is much less than that of either I or XI. It has been reported that I reacts with N-bromosuccinimide to give a single isomer of 3,7-dibromo-1,2,5,6-dibenz-1,5-cycloöctadiene (XII).[3b]


XI



XII

In the present work it was found that II reacted with two molar equivalents of N-bromosuccinimide, but no pure product could be isolated.

The ultraviolet spectrum of II in ethanol shows an absorption maximum at 235 mμ (ε 9,680) and two points of inflection at 265 and 275 mμ. Biphenyl exhibits a maximum at 249 mμ (ε 18,000) in ethanol.[13] The hypsochromic shift of the maximum of II relative to the maximum of biphenyl might be attributed to non-planarity of the biphenyl system present in II. This argument has been used in the interpretation of the spectra of other biphenyl derivatives in which the *o*- and *o'*-positions are joined by short chains of atoms.[14] In contrast to II, the ultraviolet spectrum of XI in ethanol shows a maximum at 247 mμ (ε 15,700) more like that of biphenyl. According to the argument already cited,[14] these data would indicate that the phenyl groups in XI can more readily become approximately coplanar than the phenyl groups in II. The hydrocarbon XI was conveniently prepared by the reduction of the ketone III by the Huang-Minlon modification of the Wolff–Kishner reduction.[15]

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[6] G. Schroeter, German Patent 220,852; *Chem. Zentr.*, **81**, I, 1470 (1910).

[7] R. Baltzly and J. S. Buck, THIS JOURNAL, **62**, 164 (1940).

[8] W. S. Ide and R. Baltzly, *ibid.*, **70**, 1084 (1948).

[9] D. Shapiro, *J. Org. Chem.*, **15**, 1027 (1950).

[10] E. D. Bergmann and M. Sulzbacher, *ibid.*, **16**, 84 (1951).

[11] A. Girard and G. Sandulesca, *Helv. Chim. Acta*, **19**, 1095 (1936).

[12] H. Rapoport and A. R. Williams, THIS JOURNAL, **71**, 1774 (1949).

[13] G. H. Beaven, D. M. Hall, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 854 (1952).

[14] E. A. Braude and E. S. Waight, "Progress in Stereochemistry," Vol. 1, Academic Press, Inc., New York, N. Y., 1954, p. 142. NOTE ADDED IN PROOF: Since this work was completed, ultraviolet spectra that are very similar to the spectra of I and II and are interpreted in a similar manner have been reported for carboxylic esters with the ring systems present in these hydrocarbons by G. H. Beaven, G. R. Bird, D. M. Hall, E. A. Johnson, J. E. Ladbury, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 2708 (1955).

[15] Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

The hydrocarbon II should be asymmetric, and attempts to resolve it are in progress. Preliminary attempts to convert II and the mixture of trienes Xa and Xb to 1,2,3,4-dibenzcyclooötatetraene were unsuccessful.

Experimental[16]

1,2,3,4-Dibenz-1,3-cycloheptadien-6-one (III).—2,2′-Biscyanomethylbiphenyl was prepared by heating a mixture of 68 g. of 2,2′-bis-bromomethylbiphenyl,[17] 29.3 g. of potassium cyanide, 400 ml. of acetone and 200 ml. of water to 60°. An exothermic reaction set in which was vigorous enough to cause the mixture to boil for about 10 minutes without external heating. After the exothermic reaction had subsided, the two-phase mixture was heated under reflux for 1 hour with frequent shaking. The reaction mixture was added to 2 l. of water; the orange oil which separated soon solidified. The solid was collected on a filter, dried, and crystallized from 95% ethanol using Norit. The dinitrile, m.p. 76–78°, amounted to 40.2 g. (87%). The use of aqueous acetone as a solvent avoids partial hydrolysis of the dinitrile which occurs when aqueous ethanol is used as the solvent.[18]

6-Imino-5-cyano-1,2,3,4-dibenz-1,3-cycloheptadiene was prepared from the dinitrile in 93% yield by the method of Kenner and Turner.[4] The iminonitrile was hydrolyzed to 6-imino-1,2,3,4-dibenz-1,3-cycloheptadiene-5-carboxylic acid by concentrated sulfuric acid.[4] The imino acid was not purified. A suspension of the dry, crude product in 80% phosphoric acid was hydrolyzed and decarboxylated by heating under reflux for 1 hour according to the method of Sakan and Nakazaki.[18] The yield of the ketone III, m.p. 78–79.8°, from the iminonitrile was 80%.

Ethyl Ester of 6-Hydroxy-1,2,3,4-dibenz-1,3-cycloheptadiene-6-acetic Acid (IV).—A solution of 33.3 g. of the ketone III and 28.5 g. of ethyl bromoacetate in 250 ml. of dry benzene was stirred with 11.0 g. of activated zinc.[19] An exothermic reaction began after an initial gentle warming. After the exothermic reaction had subsided, the mixture was stirred under reflux for 1.5 hours. The cooled reaction mixture was acidified with 60 ml. of 10% sulfuric acid solution, and the layers were separated. The aqueous layer was extracted with benzene, which was added to the organic layer. After the organic layer had been washed with water, saturated sodium bicarbonate solution, and saturated sodium chloride solution, the benzene was distilled under reduced pressure. Crystallization of the solid residue from hexane afforded 39.8 g. (84%) of the hydroxyester IV as large colorless prisms, m.p. 74.5–76°. For analysis a portion was recrystallized from hexane; m.p. 74.6–75.8°.

Anal. Calcd. for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.98; H, 6.67.

Hydrazide of 6-Hydroxy-1,2,3,4-dibenz-1,3-cycloheptadiene-6-acetic Acid (V).—The hydroxyester IV (39.8 g.) and 95% hydrazine (80 ml.) were heated together at 80–85° for 2 hours, then allowed to remain at room temperature for 12 hours. Excess hydrazine was distilled under reduced pressure, and the final traces were distilled at a pressure of 0.1 mm. The solid residue was crystallized from ethanol to give 33.8 g. (89%) of the hydrazide V as tiny white needles, m.p. 177–179°.

Anal. Calcd. for $C_{17}H_{18}O_2N_2$: C, 72.32; H, 6.43; N, 9.93. Found: C, 72.03; H, 6.32; N, 10.21.

1-Oxa-3-aza-7,8,9,10-dibenzspiro[4.6]undeca-7,9-diene-2-one (VI).—The hydrazide V (33.8 g.), water (200 ml.), ice (50 g.) and glacial acetic acid (20 ml.) were placed in a separatory funnel. A solution of 16.5 g. of sodium nitrite in 25 ml. of water was added, and the mixture was shaken vigorously for 20 minutes. The suspension of acid azide was extracted with benzene. The unreacted hydrazide, removed from the benzene extract by filtration, amounted to 2.57 g. The solution of acid azide was washed with water, saturated sodium bicarbonate solution, and saturated sodium chloride solution, and then dried over anhydrous magnesium sulfate. Decomposition of the acid azide was accomplished by distilling the benzene from the solution at atmospheric pressure. Final traces of benzene were distilled under reduced pressure, and the solid residue was crystallized from 95% ethanol to give 22.9 g. (78% based on the weight of hydrazide not recovered) of the oxazolidone VI, m.p. 219–222.5°. An analytical sample recrystallized from 95% ethanol melted at 221–223°.

Anal. Calcd. for $C_{17}H_{15}O_2N$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.77; H, 5.54; N, 5.18.

6-Hydroxy-6-aminomethyl-1,2,3,4-dibenz-1,3-cycloheptadiene (VII).—The oxazolidone VI (5.00 g.) and potassium hydroxide (10 g.) were heated under reflux in 150 ml. of 95% ethanol for 12 hours in an atmosphere of nitrogen. The alcohol was distilled under reduced pressure and enough 10% hydrochloric acid was added to the residue to give an acidic solution, which was heated on a steam-bath for 20 minutes and filtered while hot. The aminoalcohol hydrochloride precipitated from the cooled filtrate. The mixture was made basic by the addition of 10% sodium hydroxide solution and extracted with chloroform. After the chloroform solution had been washed with water and dried over anhydrous sodium sulfate, the solvent was distilled under reduced pressure. The residue was crystallized from benzene to give 4.07 g. (90%) of the aminoalcohol VII as small colorless needles, m.p. 143–146.5°. For analysis a portion was recrystallized from benzene; m.p. 144.6–146.3°.

Anal. Calcd. for $C_{16}H_{17}ON$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.34; H, 7.16; N, 6.04.

1,2,3,4-Dibenz-1,3-cyclooötadiene-6-one (VIII).—The aminoalcohol VII (4.07 g.) was dissolved in 35 ml. of water containing 4 ml. of glacial acetic acid. The solution was cooled in an ice-bath, and a solution of 1.3 g. of sodium nitrite in 5 ml. of water was added. Nitrogen evolution began immediately. The mixture was allowed to remain at room temperature for 12 hours, and then it was heated on a steam-bath for 1 hour. The cooled mixture was extracted with ether, and the extracts were washed with water, saturated sodium bicarbonate solution, saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The ether was distilled, and the viscous residue was dissolved in 15 ml. of absolute ethanol. Glacial acetic acid (1.5 ml.) and Girard reagent T (3.35 g.) were added, and the resulting mixture was heated under reflux for 1 hour. The cooled mixture was poured into 100 ml. of ice-water containing 1.25 g. of sodium carbonate, and the non-ketonic material was extracted with ether. The aqueous phase was acidified with 15 ml. of concentrated hydrochloric acid, and was allowed to remain at room temperature for 1.5 hours. The solid ketone which separated was extracted with ether. The ethereal solution was washed with water, saturated sodium bicarbonate solution, and saturated sodium chloride solution. The ether was distilled, and the residue was crystallized from methanol to give 1.29 g. (34%) of the ketone VIII, m.p. 108.5–111.1°. For analysis a portion was recrystallized from methanol to give VIII as long, colorless prisms, m.p. 110.9–111.6°.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.38; H, 6.29.

1,2,3,4-Dibenz-1,3-cyclooötadiene (II).—The ketone VIII (0.574 g.) and 85% hydrazine hydrate (2 ml.) were added to a solution of 1.0 g. of potassium hydroxide in 25 ml. of diethylene glycol. The mixture was heated under reflux for 1.8 hours, and then water and excess hydrazine were distilled until the temperature of the reaction mixture reached 205°. The white solid which steam distilled was dissolved in ether, which was used later for extraction. The reaction mixture was heated under reflux at 205–210° for 2.5 hours. A white solid was deposited on the cool portion of the reaction vessel during this period. After cooling, the total reaction mixture was diluted with 80 ml. of water, acidified with hydrochloric acid, and extracted with ether. After the ethereal solution had been washed with water, saturated sodium bicarbonate solution, and saturated sodium chloride solution, the ether was distilled. The residue was sublimed at 125° (0.05 mm.), and then crystallized from 95% ethanol to give 0.441 g. (82%) of the hydrocarbon II as long, colorless prisms, m.p. 151–152°.

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(16) Melting points are corrected. We are indebted to Dr. S. M. Nagy and his associates for the analyses and the ultraviolet spectra, which were determined in 95% ethanol with a Cary ultraviolet recording spectrophotometer, model 11MS.

(17) D. M. Hall, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 711 (1950).

(18) T. Sakan and M. Nakazaki, *J. Inst. Polytech., Osaka City Univ.*, **1**, No. 2, 23 (1950); *C. A.*, **46**, 5036 (1952).

(19) L. F. Fieser and W. S. Johnson, THIS JOURNAL, **62**, 575 (1940).

Anal. Calcd. for $C_{15}H_{16}$: C, 92.25; H, 7.75; mol. wt., 208. Found: C, 92.16; H, 7.61; mol. wt., 226.

1,2,3,4-Dibenz-1,3-cycloöctadiene-6-ol (IX).—A solution of sodium borohydride (0.4 g.) in 15 ml. of methanol containing one drop of 10% sodium hydroxide solution was added to a stirred solution of the ketone VIII (2.00 g.) in 30 ml. of methanol. After the resulting solution had been stirred for 2 hours at room temperature, it was diluted with 200 ml. of water. The *p*H of the aqueous phase was adjusted to 5 by the addition of 10% sulfuric acid solution, and the alcohol IX was extracted with ether. The ethereal solution was washed with water, saturated sodium bicarbonate solution and saturated sodium chloride solution, and dried over Drierite. Crystallization from ligroin of the residue obtained on distillation of the ether afforded 1.73 g. (86%) of the alcohol IX as white needles, m.p. 95–97°. A portion recrystallized from ligroin had m.p. 96.5–97.5°.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.71; H, 7.29.

Dehydration of 1,2,3,4-Dibenz-1,3-cycloöctadiene-6-ol.—The alcohol IX (1.54 g.) and boric acid (0.5 g.) were placed in a short-path distillation apparatus. The mixture was heated gradually to 270–275°, while the pressure was slowly reduced to 0.1 mm., and these conditions were maintained for 30 minutes. The distillate, which quickly solidified, was crystallized from 95% ethanol to give 0.771 g. (55%) of a mixture of the isomeric olefins Xa and Xb, m.p. 88–109°. Recrystallization did not narrow the melting range, nor did treatment of the mixture with sodium ethoxide in boiling ethanol for 18 hours give a single pure isomer.

Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.10; H, 7.15.

A portion of the olefin mixture (0.117 g.) was hydrogenated at atmospheric pressure and room temperature in 15 ml. of glacial acetic acid in the presence of 0.4 g. of 10% palladium-on-carbon. After 30 minutes, 99% of one molar equivalent of hydrogen had been absorbed. The catalyst was removed by filtration, and the solvent was distilled under reduced pressure. The residue was sublimed at 120° (0.3 mm.) and crystallized from 95% ethanol to give 0.095 g. (81%) of the hydrocarbon II, m.p. 150–151.5°. After recrystallization from 95% ethanol the melting point was 150.5–151.1°. The infrared spectrum of the hydrogenation product was identical with that of an authentic sample of II obtained by Wolff–Kishner reduction of VIII and mixed melting point showed no depression.

1,2,3,4-Dibenz-1,3-cycloheptadiene (XI).—The ketone III (0.50 g.) and 85% hydrazine hydrate (2 ml.) were added to a solution of 1.0 g. of potassium hydroxide in 10 ml. of diethylene glycol. The mixture was heated under reflux for 2 hours, and then water and excess hydrazine were distilled until the temperature of the reaction mixture reached 200°. The distillate was extracted with ether, which was used later for extractions. The reaction mixture was heated under reflux at 200° for 3 hours, and then cooled and diluted with 80 ml. of water. After the mixture had been acidified with hydrochloric acid, it was extracted with ether, and the ethereal solution was washed with water, saturated sodium bicarbonate solution and saturated sodium chloride solution. The ether was distilled, and the residue was distilled in a short-path apparatus at 90–100° (0.1 mm.). The distillate solidified and was crystallized from methanol to give 0.235 g. (50%) of the hydrocarbon XI, m.p. 39.8–40.8°.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DE PAUL UNIVERSITY]

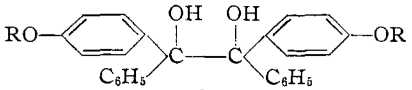
Pinacol Rearrangement of *sym-p,p'*-Dialkoxybenzopinacols

BY ROBERT P. ZELINSKI[1] AND MYRON JURSICH

RECEIVED AUGUST 10, 1955

Four *sym-p,p'*-dialkoxybenzopinacols have been prepared by two bimolecular reduction procedures and subjected to the pinacol rearrangement. The migrational aptitudes of the *n*-propoxy-, *n*-butoxy-, *n*-amyloxy- and isoamyloxyphenyl groups all fall in the range 93–95%.

The migrational aptitudes of the *p*-methoxy- and the *p*-ethoxyphenyl groups are known to be very high in the pinacol rearrangement of *sym*-pinacols (I).[2,3] Similar results are now reported for four larger alkoxyl groups.



I

These benzopinacols were prepared by the bimolecular reduction of *p*-alkoxybenzophenones using as reducing agents both magnesium and iodine,[4] and zinc and acetic acid.[3,5] Both procedures were satisfactory, but the second was more convenient. The *p*-alkoxybenzophenones were prepared by benzoylating appropriate alkyl phenyl ethers[6] and more satisfactorily by alkylating *p*-hydroxybenzophenone.[7]

The pinacol rearrangement was done by boiling in acetic acid with a little iodine,[8] but the alkoxybenzopinacolones could not be separated. Therefore, the migrational aptitudes were determined according to Bailar's[8] procedure in which the pinacolones are not isolated, but are cleaved by alcoholic alkali to triarylmethanes and arylcarboxylic acids. The neutral equivalent of the acid permits calculation of the mole percentages of benzoic and *p*-alkoxybenzoic acids so formed and of the relative migrational aptitudes of the *p*-alkoxyphenyl group. The results (Table I) for all four alkoxyphenyls are comparable to the 98.3 and 98.6% previously reported for *p*-methoxy- and *p*-ethoxyphenyl.[2,3] We believe that the difference between our values

TABLE I

MIGRATIONAL APTITUDES OF *p*-ALKOXYPHENYL GROUPS

Alkoxy	Eq. wt. of acid mixt.	Migrational aptitude
Methoxy[2]		98.6
Ethoxy[3]		98.3
n-Propoxy	125.5	94.1
n-Butoxy	126.8	94.0
n-Amyloxy	127.0	95.1
i-Amyloxy	128.6	93.4

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(1) Research Center, Phillips Petroleum Co., Bartlesville, Okla.

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