was immediately extracted with approximately 500 ml. of ether in a continuous extractor for 26 hours at room temperature. At the end of this time the ether solution was cooled and shaken with 500 ml. of Brady reagent[24] for 10 minutes. The ether was removed at room temperature under an air jet and the insoluble 2,4-dinitrophenylhydrazones which precipitated were removed by filtration on a fritted glass filter; weight 450 mg.

Chromatography of the 2,4-Dinitrophenylhydrazones.—The crude mixture of 2,4-dinitrophenylhydrazones was dissolved in a 1:2 (by volume) benzene–petroleum ether (b.p. 60–90°) mixture and chromatographed after the manner of Roberts and Green[33] on silicic acid[25]–Celite[26] (3:1 by weight) on a 43 × 250 mm. column. The column was washed with 200 ml. of 1:1 (by volume) benzene–petroleum ether (b.p. 60–90°) and then developed with 75 ml. of benzene containing 0.5 ml. of *t*-butyl alcohol per liter. The column showed the following bands: A, orange-red in color, approximately 3 cm. in width at a distance of approximately 3 cm. from the top of the column; B, orange-yellow in color, approximately 1.5 cm. in width and 8 cm. from the top of the column; C, orange in color, approximately 2 cm. in width and 10.5 cm. from the top of the column; D, orange in color, approximately 3 cm. in width and approximately 13 cm. from the top of the column. The column was extruded and the zones cut and eluted with ethanol.

Identification of Chromatographically Separated 2,4-Dinitrophenylhydrazones.—The contents of each zone was crystallized from ethanol. The empirical formulas and physical constants[34] showed the compounds to be the 2,4-dinitrophenylhydrazones of furfuraldehyde, formaldehyde, crotonaldehyde and acetaldehyde. A mixed melting point confirmed the identity of the compounds.

Identical results were obtained when D-xylose, D-lyxose and D-ribose were treated in the same way.

Acknowledgment.—We wish to thank Mrs. P. P. Wheeler for the microanalyses and Mr. L. S. Hafner for technical assistance, and to thank Dr. C. Schuerch of the State University of New York, College of Forestry, for his helpful criticism of the manuscript.

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[33] J. D. Roberts and Charlotte Green, *Ind. Eng. Chem., Anal. Ed.*, **18**, 335 (1946).

[34] J. D. Roberts and Charlotte Green, THIS JOURNAL, **68**, 214 (1946); E. H. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945).

INDIAN HEAD, MD.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, NORTHWESTERN UNIVERSITY]

The Stereoisomers of 10-Hydroxymethyl-2-decalol[1]

BY L. S. MINCKLER, A. S. HUSSEY AND ROBERT H. BAKER

RECEIVED AUGUST 15, 1955

The preparation of the four stereoisomers of 10-hydroxymethyl-2-decalol starting from 10-carbethoxy-γ-$\Delta^{1,9}$-2-octalone is described. Configurational assignments for each of these isomers are made.

In an earlier communication having to do with the stereochemistry of angularly substituted methyldecalols,[2] we described a 10-hydroxymethyl-2-decalol which melted at 142°. This was derived from a 10-carboxy-2-decalol which readily formed a lactone; hence the hydroxymethyl and hydroxyl groups were known to be *cis* to one another. The ring fusion of this series of compounds recently has been shown to be *trans*.[3-5] As a consequence, this diol is now correctly designated *cis*-10-hydroxymethyl-2-*trans*-decalol[6] (I). We describe here the synthesis and configurational assignment of the other three isomeric diols: *trans*-10-hydroxymethyl-2-*trans*-decalol (II), *cis*-10-hydroxymethyl-2-*cis*-decalol (III) and *trans*-10-hydroxymethyl-2-*cis*-decalol (IV). All of these have been prepared from the same starting material, 10-carbethoxy-$\Delta^{1,9}$-2-octalone (V).[2,3,7]

The *trans–trans*-diol II was obtained in the following way. 10-Carbethoxy-2-*trans*-decalone (VI),[2,3,7] from V by catalytic reduction, was reduced with sodium borohydride to an hydroxyester. This hydroxyester could be converted to the hydroxyacid and the lactone previously described[2,3,5] by saponification, or to I by reduction with lithium aluminum hydride. It was therefore *cis*-10-carbethoxy-2-*trans*-decalol (VII). *trans*-10-Carbethoxy-2-*trans*-decalol was obtained as its acetate ester VIII when the *p*-toluenesulfonate derivative of VII was treated with potassium acetate in acetic acid. Reduction of VIII with lithium aluminum hydride gave *trans*-10-hydroxymethyl-2-*trans*-decalol (II), m.p. 117.5–119°. A second crystalline modification of II melted at 128–129°, re-melted at 117–118°.

The *cis–cis*-diol III was obtained from V simply by varying the order of the steps which lead to I[2]. Reduction of V to *cis*-10-hydroxymethyl-$\Delta^{1,9}$-2-octalol (IX) by means of lithium aluminum hydride was followed by catalytic reduction to an hydroxymethyldecalol, m.p. 124–125°. This diol was different from I or II, and that it was the *cis–cis* diol III was confirmed in the following way. With sodium borohydride, V was reduced to the hydroxyester X. When X was reduced catalytically to the decalin derivative and the latter, without isolation, treated with lithium aluminum hydride, compound I was formed. When X was treated in the reverse order (that is, with lithium aluminum hydride and then reduced catalytically), the diol which melts at 124–125° was obtained. This diol must therefore have a *cis* relationship of hydroxymethyl and hydroxyl groups and a *cis* ring fusion.

The *trans–cis*-diol IV was obtained from V by still another variation in the order of the steps. The keto group was first blocked by the formation of the dioxolan derivative XI.[5,8] The ester function

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[1] We acknowledge with gratitude a grant from the Research Corporation which made this investigation possible.

[2] A. S. Hussey, H. P. Liao and R. H. Baker, THIS JOURNAL, **75**, 4727 (1953).

[3] W. G. Dauben, R. C. Tweit and R. L. MacLean, *ibid.*, **77**, 48 (1955).

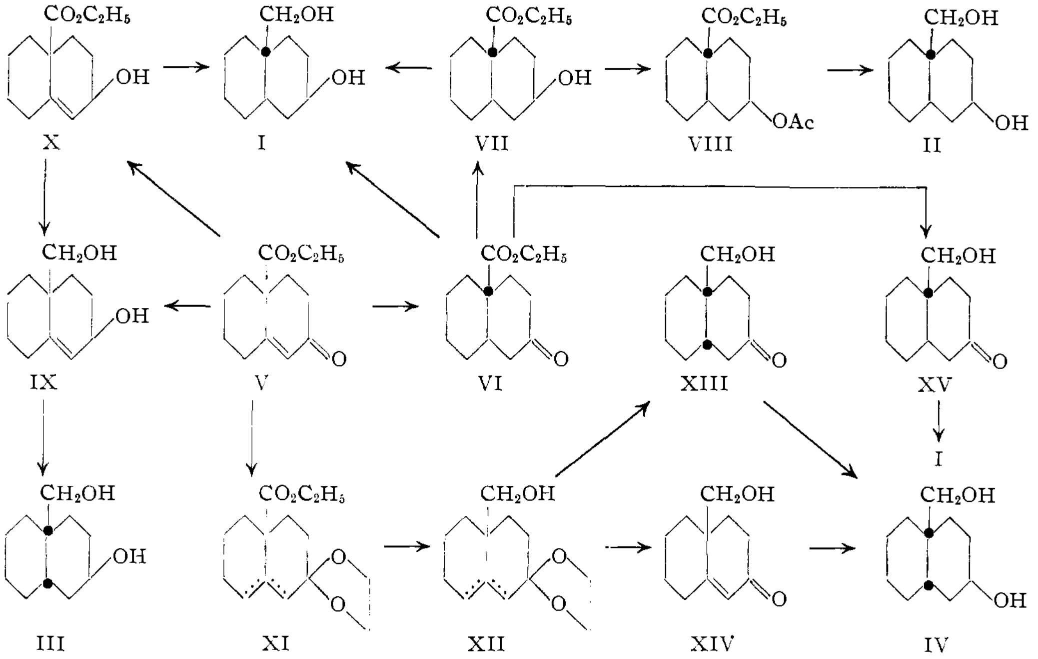
[4] A. S. Dreiding and A. J. Tomasewski, *ibid.*, **77**, 168 (1955).

[5] A. S. Dreiding and A. J. Tomasewski, *ibid.*, **77**, 411 (1955).

[6] The relationship of angular and peripheral substituents is expressed as a prefix to the name; the nature of the ring fusion as a prefix to the root of the name.

[7] E. C. duFeu, F. J. McQuillen and R. Robinson, *J. Chem. Soc.*, 53 (1937).

[8] M. Idelson, R. L. Kronenthal and E. I. Becker, Abstract of Papers, Cincinnati Meeting of the American Chemical Society, March 29–April 7, 1955, p. 49N.



was then reduced with lithium aluminum hydride to furnish 10-hydroxymethyl-$\Delta^{1,9?}$-2-octalone-2-dioxolan (XII). Reduction over palladium–charcoal followed by hydrolysis furnished 10-hydroxymethyl-2-*cis*-decalone (XIII) and the latter with sodium borohydride gave the *trans–cis*-diol IV, m.p. 139–140°, as the principal product. A small amount of *cis–cis*-diol III was isolated as its bis-*p*-nitrobenzoate derivative. Reduction of XIII with lithium aluminum hydride, or catalytically, appeared to give a slightly higher ratio of IV to III.

The same diol, IV, was obtained when XII was first hydrolyzed to 10-hydroxymethyl-$\Delta^{1,9}$-2-octalone (XIV) and the latter then catalytically reduced. Two moles of hydrogen were rapidly absorbed to form IV directly.

The nature of the ring fusion established by catalytic reduction of the angularly substituted octalin derivatives merits comment. When the angular group is methyl[7] or dichloromethyl[9] a *cis* ring fusion results from catalytic reduction of the $\Delta^{1,9}$-2-octalone compound. When the angular group is carbethoxy, a *trans* ring fusion results.[2,3,8] It has been established that some of the other ring fusion isomer is simultaneously formed when the angular group is methyl.[10] Our experience with the other angular groups suggests that the second isomer is a very minor product. When the angular group is hydroxymethyl, the principal product is the one which has a *cis* ring fusion. However, the properties of the crude products, including infrared spectra, indicate that the reduction is less stereospecific than it is with the other angular groups above.

It has been suggested that such angularly substituted compounds are slightly more stable in the *cis* configuration,[4,11] or in the *trans* configuration.[12] The factors which direct catalytic reduction to the formation of either a *cis* or a *trans* ring fusion are not clear.

The reduction of the 2-keto group to an hydroxyl group, once the ring fusion has been established, appears to following confirmational concepts as generalized by Barton[13] and Siegel.[14] Thus, 10-methyl-2-*trans*-decalone gave mainly *cis*-10-methyl-2-*trans*-decalol[4] and 10-hydroxymethyl-2-*trans*-decalone (XV) gave mainly I. In both of these products the hydroxyl group is equatorial. Similarly XIII and XIV gave IV. This last fact lends support to our earlier assignment of *trans*-10-methyl-2-*cis*-decalol to the product of the catalytic reduction of 10-methyl-2-*cis*-decalone.[2] Such reductions in the *cis* ring-fused series appear to be less stereospecific than in the *trans* ring-fused series, however.

The reduction of the 2-keto group in the octalin series, which produces an hydroxyl group *cis* to the angular group as in IX or X, can be ascribed to the planar character of the $\Delta^{1,9}$-octalin ring system which makes the *cis* configuration the more favored equatorial one.

Experimental[15,16]

***cis*-10-Carbethoxy-2-*trans*-decalol (VII).**—A solution of 0.72 g. (0.019 mole) of sodium borohydride in 40 cc. of ethanol was added to 8.4 g. (0.0375 mole) of 10-carbethoxy-2-*trans*-decalone[2,3,7] in 40 cc. of ethanol. The mixture was allowed to stand at room temperature for 12 hours, then was neutralized with 4.56 cc. of acetic acid. The solvent was partly removed at the water-pump. Several ether extracts of the residue were combined, washed with water, dried and distilled under reduced pressure. There was thus obtained 7.6 g. (90%) of VII, b.p. 110–113° at 0.3 mm., $n^{25}D$ 1.4890.

Anal. Calcd. for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.9; H, 9.5.

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[9] R. B. Woodward, THIS JOURNAL, **62**, 1208 (1940).

[10] R. B. Woodward, *et al.*, *ibid.*, **74**, 4223 (1952).

[11] W. E. Bachmann, A. Ross, A. S. Dreiding and P. A. S. Smith, *J. Org. Chem.*, **19**, 222 (1954).

[12] R. B. Turner, THIS JOURNAL, **74**, 2118 (1952); see also ref. 10, p. 4224.

[13] D. H. R. Barton, *Experientia*, **6**, 316 (1950); *J. Chem. Soc.*, 1027 (1953).

[14] S. Siegel, THIS JOURNAL, **75**, 1317 (1953).

[15] "Microanalyses" by Miss Hildegarde Beck, Microanalytical Laboratory, Chemistry Department, Northwestern University.

[16] All melting points observed on a micro melting stage with polarizing microscope, 6X and 12X, uncorrected.

With 0.5 g. (0.013 mole) of lithium aluminum hydride in refluxing ether for 3 hours, 1.00 g. (0.0044 mole) of VII gave 0.49 g. (60%) of *cis*-10-hydroxymethyl-2-*trans*-decalol[2] (I), m.p. 141–142°, after treatment with 1.0 cc. of water and filtration of the inorganic salts.

With 3.00 g. (0.0158 mole) of recrystallized *p*-toluenesulfonyl chloride in 42 cc. of pyridine at 0° for 2 days, 3.00 g. (0.0133 mole) of VII gave 4.8 g. (95%) of the *p*-toluenesulfonate derivative, m.p. 67–75°, when the mixture was poured onto ice. An analytical sample melted at 78–79°, from ethanol.

Anal. Calcd. for $C_{20}H_{28}O_5S$: C, 63.14; H, 7.42. Found: C, 63.1; H, 7.2.

***trans*-10-Carbethoxy-2-*trans*-decalyl Acetate** (**VIII**).—A solution composed of 3.34 g. (0.0088 mole) of the *p*-toluenesulfonate ester of VII and 3.34 g. (0.0341 mole) of fused potassium acetate in 100 cc. of glacial acetic acid was refluxed for 16 hours. Most of the acetic acid was removed by distillation at 15 mm. pressure. Combined ether extracts of the residue were washed, dried and distilled. A lower-boiling fraction (b.p. 70–81° at 1.0 mm., n^{25}_D 1.4767, 0.67 g.) and a higher boiling fraction (b.p. 110–113° at 1.0 mm., n^{25}_D 1.4739, 1.09 g.) were collected. An infrared spectrum of the former had the characteristic absorption band for carbon unsaturation at 6.15 μ and it was assumed to be a 10-carbethoxy-*trans*-octalin, yield 37%. The higher boiling fraction represented a 47% yield of VIII.

***trans*-10-Hydroxymethyl-2-*trans*-decal**ol (**II**).—With 0.4 g. (0.01 mole) of lithium aluminum hydride in 150 cc. of refluxing ether for 12 hours, 1.00 g. (0.0037 mole) of VIII gave 0.67 g. of semi-solid residue after treatment with 1.0 cc. of water and filtration of the inorganic salts. A chloroform solution was chromatographed on alumina. Four middle fractions crystallized when the solutions were concentrated. The crystals from the second of these melted at 128–129°, re-melted at 115–116°; the crystals from the other three fractions melted at 115–117°. Combination of all of these fractions and recrystallization from chloroform gave 0.47 g. (69%) of II, m.p. 117.5–119°. By minor variations in the recrystallization procedure, or by seeding, the crystalline modification melting at 128–129° could occasionally be obtained. Such samples always re-melted at 117–118°.

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 formed readily in pyridine in 96% yield, m.p. 225°. An analytical sample melted at 226°, from ethanol (very slightly soluble).

Anal. Calcd. for $C_{25}H_{26}O_8N_2$: C, 62.23; H, 5.43; N, 5.81. Found: C, 62.4; H, 5.3; N, 6.0.

***cis*-10-Hydroxymethyl-$\Delta^{1,9}$-2-octal**ol (**IX**).—With 2.66 g. (0.0700 mole) of lithium aluminum hydride in 200 cc. of refluxing ether for 6 hours, 10.00 g. (0.045 mole) of 10-carbethoxy-$\Delta^{1,9}$-2-octalone[2,7] gave 7.00 g. (85%) of IX, m.p. 115–118°, after decomposition of the excess reducing agent with 6 cc. of water, filtration of the inorganic salts and concentration of the ether solution. An analytical sample melted at 119–120°, from chloroform.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.0; H, 9.8.

***cis*-10-Hydroxymethyl-2-*cis*-decal**ol (III).—In 110 cc. of ethanol over 0.3 g. of platinum oxide under one atmosphere of hydrogen, 5.50 g. (0.0302 mole) of IX gave 4.86 g. (88%) of III after crystallization from chloroform–hexane, m.p. 121–123°. An analytical sample melted at 124–125°, from chloroform.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.6; H, 10.9.

The bis-*p*-nitrobenzoate was prepared in pyridine, 90%, m.p. 134–136°. An analytical sample melted at 136–137° from ethanol.

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

***cis*-10-Carbethoxy-$\Delta^{1,9}$-2-octal**ol (**X**).—A solution of 1.5 g. (0.04 mole) of sodium borohydride in 75 cc. of methanol was added to 20.0 g. (0.090 mole) of 10-carbethoxy-$\Delta^{1,9}$-2-octalone[2,7] in 75 cc. of methanol. The mixture stood at room temperature for 12 hours, then was neutralized with 10.0 cc. of acetic acid. The solvent was partly removed at the water-pump. Several ether extracts of the residue were combined, washed, dried and distilled. There was obtained 19.0 g. (95%) of X, b.p. 124–134° at 1.8 mm., n^{21}_D 1.5035. A sample for analysis was redistilled at 120° at 1 mm., n^{25}_D 1.5025.

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 70.1; H, 9.1.

With 0.25 g. of lithium aluminum hydride in refluxing ether in the usual manner, 1.00 g. of X furnished 0.61 g. (75%) of IX, m.p. 115–117°, no depression.

When reduced over 50 mg. of platinum oxide at atmospheric pressure in 15 cc. of ethanol, 0.82 g. (3.7 millimoles) of X absorbed the theoretical amount of hydrogen. The catalyst and solvent were removed and the residue was reduced in the usual way with lithium aluminum hydride. There was thus obtained 0.25 g. (38%) of I, m.p. 140–142°, no depression. The hydroxyester product of a second catalytic reduction of X was saponified and furnished *cis*-10-carboxy-2-*trans*-decalol,[2,3,5] m.p. 161.5°.

10-Carbethoxy-$\Delta^{1,9?}$-2-octalone-2-dioxolan (**XI**).—A solution of 13.6 g. (0.061 mole) of 10-carbethoxy-$\Delta^{1,9}$-2-octalone[2,7] in 125 cc. of benzene with 8.0 g. (0.13 mole) of ethylene glycol and 0.2 g. of *p*-toluenesulfonic acid was refluxed for 5 hours through a column which separated water as formed.[5,8] The benzene solution was washed with sodium bicarbonate solution. The residue remaining after distilling the solvent gave 15.3 g. (95%) of crude product, b.p. 106–120° at 0.4 mm., n^{25}_D 1.4994. Redistillation gave 14.5 g. (90%) of XI, b.p. 115–116° at 0.4 mm., n^{25}_D 1.4996.

Anal. Calcd. for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 68.1; H, 7.9.

This material could not be hydrogenated over platinum oxide in ethanol at one atmosphere.

10-Hydroxymethyl-$\Delta^{1,9?}$-2-octalone-2-dioxolan[8] (**XII**).—An ether solution of 11.00 g. (0.0414 mole) of XI in 100 cc. of ether was added slowly to 2.5 g. (0.066 mole) of lithium aluminum hydride in 100 cc. of ether. The reaction mixture was refluxed for 13 hours before the product was isolated in the usual way. Distillation gave 8.80 g. (95%) of XII, b.p. 132–134° at 0.4 mm., n^{25}_D 1.5297. This very viscous material crystallized on standing, m.p. 78–90°, but was not further purified.

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.9; H, 8.4.

10-Hydroxymethyl-2-*cis*-decalone (**XIII**).—A sample of the unsaturated dioxolan XII (4.20 g., 0.0191 mole) was reduced over 10% palladium-on-charcoal catalyst in a modified Parr apparatus at low pressure, using ethanol as solvent.[8] One mole of hydrogen was absorbed. Catalyst and solvent were removed and the residue was distilled. The product, which was collected over the range 145–150° at 0.05 mm., was a colorless, extremely viscous liquid having n^{25}_D 1.5160. The presence of carbonyl impurity was indicated by strong absorption at 5.86 μ. The yield was 3.75 g., 90%.

Anal. Calcd. for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 70.0; H, 9.9.

Ethylene glycol appeared in the forerun when purification by re-distillation was attempted and some polymeric material was left as pot-residue. Consequently, further purification of the dioxolan was not attempted. Instead, the material was hydrolyzed by 3 hours at reflux in 50 cc. of 65% aqueous methanol containing 3 cc. of concentrated hydrochloric acid. Water was added and the product was extracted with pentane. Distillation of the dried pentane solution gave 2.40 g. (80%) of 10-hydroxymethyl-2-*cis*-decalone (XIII), b.p. 134° at 0.6 mm., n^{25}_D 1.5178.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.6; H, 10.0.

A 2,4-dinitrophenylhydrazone derivative melted at 122–123.5° after recrystallization from ethanol.

Anal. Calcd. for $C_{17}H_{22}O_5N_4$: N, 15.46. Found: N, 15.5.

10-Hydroxymethyl-$\Delta^{1,9}$-2-octalone (**XIV**).—A second sample of the unsaturated dioxolan XII (2.50 g., 0.011 mole) was hydrolyzed by 1 hour at reflux in 35 cc. of methanol to which 20 cc. of 10% hydrochloric acid had been added. An ether extract furnished 1.30 g. (65%) of XIV as pale yellow crystals, m.p. 77.5–78.5°, when the solvent evaporated. A sample for analysis melted at 78.5–79.5°, from hexane–ether.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.6; H, 8.6.

***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]

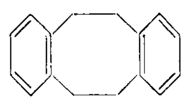
Cyclic Polyolefins. XXXIX. 1,2,3,4-Dibenz-1,3-cyclooöctadiene

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



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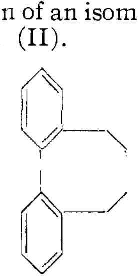

II

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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