

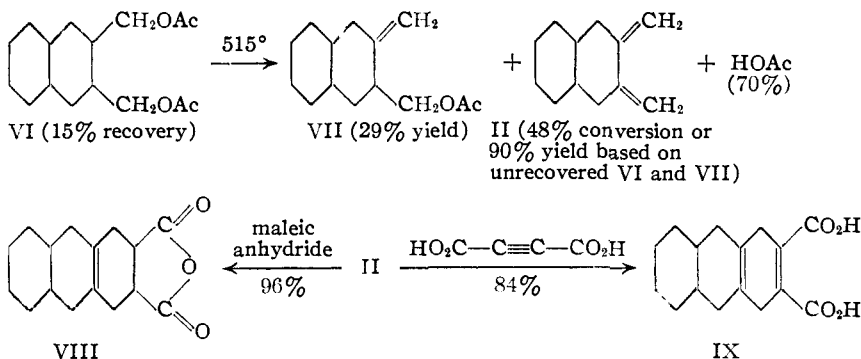
[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, WAYNE UNIVERSITY AND THE UNIVERSITY OF MARYLAND]

Cyclic Dienes. X. 2,3-Dimethylenedecalin^{1,2}BY WILLIAM J. BAILEY,³ CHIEN-WEI LIAO⁴ AND GEORGE H. COLEMAN

RECEIVED JULY 21, 1954

2,3-Dimethylenedecalin was synthesized from 1,2-dimethylenecyclohexane in a five-step procedure for ascending a series by the addition of a cyclohexane ring in an over-all yield of 68%. The final step, the pyrolysis of a diacetate, was carried out in 90% yield. The structure of this diene was proved by analysis, ultraviolet and infrared absorption, and conversion to a known derivative through an intermediate Diels-Alder adduct.

It was shown previously that 1,2-dimethylenecyclohexane (I) polymerized to a high molecular weight all-*cis* diene polymer⁵ that melted at 165°, even though the basic polymer chain is very similar to that of natural rubber. Since one essential difference between this poly-1,2-dimethylenecyclohexane and natural rubber was the presence of the ring, it was of interest to determine the effect of a cyclohexane ring on the properties of an all-*cis* polymer. One possible approach to this determination was to synthesize a monomer, such as 2,3-dimethylenedecalin (II), which contains an additional cyclohexane ring and to study the polymer derived from it. Since the cyclic diene I had been previously converted to pentacene by a very convenient three-step synthesis in 30% yield,⁶ 2,3-dimethylenedecalin (II) appeared to be an excellent starting material for other linear condensed polynuclear hydrocarbons, such as heptacene and hexacene.



By the application of a method that had been developed previously for ascending a series by the addition of a fused cyclohexane ring,⁷ 2,3-dimethylenedecalin (II) was synthesized from 1,2-dimethylenecyclohexane (I)⁸ in a five-step synthesis in an over-all yield of 68%. Thus, the cyclic diene I plus maleic anhydride produced the Diels-Alder adduct, $\Delta^9(10)$ -octahydronaphthalene-2,3-dicarboxylic anhydride (III), in 99% yield. Reduction of III with lithium aluminum hydride, followed by careful acidification of the reaction mixture, produced a 97% yield of 2,3-dimethylol- $\Delta^9,10$ -octalin (IV).

(1) Previous paper in this series, *THIS JOURNAL*, **77**, 73 (1955).

(2) Presented in part before the Division of Polymer Chemistry at the 121st Meeting of the American Chemical Society, Chicago, Ill., September, 1953.

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(5) W. J. Bailey and H. R. Golden, *THIS JOURNAL*, **76**, 5418 (1954).

(6) W. J. Bailey and M. Madoff, *ibid.*, **75**, 5603 (1953).

(7) W. J. Bailey, J. Rosenberg and L. J. Young, *ibid.*, **76**, 2251 (1954).

(8) W. J. Bailey and H. R. Golden, *ibid.*, **75**, 4780 (1953).

Acetylation of IV gave 2,3-di-(acetoxymethyl)- $\Delta^9(10)$ -octalin (V) in 90% yield. V was converted by catalytic hydrogenation to the saturated 2,3-di-(acetoxymethyl)-decalin (VI) in an 87% yield.

It had been shown that if pyrolysis conditions were selected so that no carbonization occurred in the column highly strained olefins, such as 1,2-dimethylene-4-cyclohexane, an isomer of the aromatic *o*-xylene, could be prepared pure in high yields.⁹

It was found that the diacetate VI could be pyrolyzed so that 70% of 2 moles of acetic acid was liberated at 515° without the occurrence of carbonization in the process. Under these optimum conditions the pyrolysis of VI resulted in a 48% conversion to 2,3-dimethylenedecalin (II) plus a 29% yield of the monoacetate VII and a 15% recovery of the diacetate VI. The yield of the diene II, based on unrecovered monoacetate VII and starting material VI, was 90%. If more acetic acid was

liberated, carbonization took place and a lower yield (based on unrecovered material) of a less pure diene was obtained.

The structure of 2,3-dimethylenedecalin (II) was proved by analysis, ultraviolet and infrared absorption and conversion to known derivatives through intermediate Diels-Alder adducts. II did not show a maximum or minimum in its ultraviolet absorption spectrum above 220 $m\mu$ but appeared to

reach a maximum just below 220 $m\mu$, which indicated the presence of conjugated double bonds. 1,2-Dimethylenecyclohexane (I) possesses a maximum at 220 $m\mu$.⁸ Strong absorption bands in the infrared spectrum at 895, 1450 and 2900 cm^{-1} confirm the structure of II. In Diels-Alder reactions, 2,3-dimethylenedecalin (II) was allowed to react with maleic anhydride to produce a 96% yield of $\Delta^4a(10a)$ -dodecahydroanthracene-2,3-dicarboxylic anhydride (VIII) and with acetylenedicarboxylic acid to produce an 84% yield of $\Delta^{2,4a(10a)}$ -decahydroanthracene-2,3-dicarboxylic acid (IX). Simultaneous decarboxylation and dehydrogenation of IX produced the known anthracene. Other reactions of this interesting cyclic diene will be reported later.

Experimental¹⁰

2,3-Dimethylol- $\Delta^9(10)$ -octalin (IV).—To a 5-liter, three-necked flask, equipped with a stirrer and a condenser and

(9) W. J. Bailey and J. Rosenberg, *ibid.*, **77**, 73 (1955).

(10) All melting points are corrected. The authors are indebted to Vivian Kapuscinski for the analyses.

containing a solution of 90 g. (2.34 moles) of lithium aluminum hydride in 200 ml. of dry ether, 340 g. (1.65 moles) of $\Delta^9(10)$ -octahydronaphthalene-2,3-dicarboxylic anhydride (III)⁹ was added. The addition was made over a period of 3 days by means of an exhaustive extractor. It was found that a lower yield of the glycol IV was obtained if the solid anhydride III was added in small quantities through a flexible rubber tube. After the reaction mixture was heated under reflux for an additional day, the excess of lithium aluminum hydride was destroyed cautiously by the dropwise addition of water. The lithium-aluminum-glycol complex was decomposed by the slow addition of 4300 ml. of 5% hydrochloric acid, with vigorous stirring. Care was taken to ensure that the pH of the solution was always above 2. After the ether layer was separated, the aqueous layer was extracted once with ether in a separatory funnel and then with ether in an exhaustive extractor. The ether extracts from these operations were combined with the original ether layer, and the resulting solution was dried over anhydrous sodium carbonate. After the ether was removed by evaporation, the residue was recrystallized from ether to obtain 310 g. (97%) of 2,3-dimethylol- $\Delta^9(10)$ -octalin (IV), m.p. 86.0–86.5°.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 73.42; H, 10.27. Found: C, 73.37; H, 10.44.

2,3-Di-(acetoxymethyl)- $\Delta^9(10)$ -octalin (V).—To a mixture of 330 g. (1.68 moles) of 2,3-dimethylol- $\Delta^9(10)$ -octalin (IV) and 300 ml. of glacial acetic acid, in a 5-liter, three-necked flask, provided with a dropping funnel and a reflux condenser, 1150 ml. of acetic anhydride was added dropwise over a 40-minute period, during which the reaction mixture was heated under reflux. The mixture was then heated under reflux for an additional 3 days to obtain a dark-red solution. After most of the acetic acid and excess acetic anhydride were removed under slightly reduced pressure, the residual liquid was fractionated through a 1.5 × 15 cm. Vigreux column to yield 374 g. (90%) of 2,3-di-(acetoxymethyl)- $\Delta^9(10)$ -octalin (V), b.p. 154–155° (2 mm.), n_D^{25} 1.4931 and d_4^{25} 1.093.

Anal. Calcd. for $C_{18}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.22; H, 8.76.

2,3-Di-(acetoxymethyl)-decalin (VI).—2,3-Di-(acetoxymethyl)- $\Delta^9(10)$ -octalin (V) (94 g., 0.33 mole) was placed in the 500-ml. liner of an Aminco high pressure hydrogenation bomb with 10 g. of W-2 Raney nickel catalyst,¹¹ and the bomb was filled with hydrogen to a pressure of 1500 pounds per square inch at 200°. A total uptake of 0.35 mole (106%) of hydrogen was observed. After the mixture was cooled overnight, the catalyst in the hydrogenated product was filtered off and the filtrate was distilled through a 1.5 × 15 cm. Vigreux column to yield 82 g. (87%) of the 2,3-di-(acetoxymethyl)-decalin (VI), b.p. 156–160° (1.6 mm.), n_D^{25} 1.4879 and d_4^{25} 1.0812.

Anal. Calcd. for $C_{18}H_{24}O_4$: C, 68.09; H, 9.20. Found: C, 68.06; H, 9.22.

2,3-Dimethylenedecalin (II).—At the rate of 1.3 g. per minute, 109 g. (0.39 mole) of 2,3-di-(acetoxymethyl)-decalin (VI) was dropped through a vertical Vycor tube, packed with 1/16-inch Pyrex helices. The tube was externally heated at 515° and was flushed continuously with a slow stream of dry, oxygen-free nitrogen, as described pre-

viously.¹ The pyrolysate passed from the tube, through a 6-inch, spiral condenser, into a receiving flask which contained about 50 mg. of 1,3,5-trinitrobenzene and which was immersed in a Dry Ice-acetone-bath. An ether solution of the pyrolysate was extracted with four 50-ml. portions of distilled water. (Titration of aliquot portions of the combined aqueous washings indicated the liberation of 75% of two molar equivalents of acetic acid.) After the ether layer was dried over anhydrous sodium carbonate, the ether was removed by evaporation. Distillation of the residue through a 6-inch, helix-packed column produced 25 g. (29%) of olefin acetate VII; 30 g. (48%) of 2,3-dimethylenedecalin (II), b.p. 130° (70 mm.), n_D^{25} 1.5025, d_4^{25} 0.9210; and 17 g. (15% recovery) of the unreacted diacetate VI. The yield of the diene II, based on unrecovered diacetate VI and olefin acetate VII, was 90%.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.80; H, 11.20. Found: C, 88.80; H, 11.19.

$\Delta^{4,6(10a)}$ -Dodecahydroanthracene-2,3-dicarboxylic Anhydride (VIII).—A solution of 1.6 g. (0.01 mole) of 2,3-dimethylenedecalin (II) and 1.0 g. (0.01 mole) of maleic anhydride in 20 ml. of ether was heated under reflux for 3 hours. After the reaction mixture was cooled, white crystals were filtered off. The crude solid was recrystallized from ether to yield 2.5 g. (96% yield) of $\Delta^{4,6(10a)}$ -dodecahydroanthracene-2,3-dicarboxylic anhydride (VIII), m.p. 196–197°.

Anal. Calcd. for $C_{18}H_{20}O_5$: C, 73.78; H, 7.84. Found: C, 73.62; H, 7.60.

$\Delta^{2,4a(10a)}$ -Decahydroanthracene-2,3-dicarboxylic Acid (IX).—A solution of 1.6 g. (0.01 mole) of 2,3-dimethylenedecalin (II) and 1.1 g. (0.01 mole) of acetylenedicarboxylic acid in 30 ml. of ether was heated under reflux for 10 hours. After the reaction mixture was cooled, a pale-yellowish solid precipitated from the solution. This solid was filtered off and recrystallized from acetone and petroleum ether (30–60°) to yield 2.3 g. (84%) of $\Delta^{2,4a(10a)}$ -decahydroanthracene-2,3-dicarboxylic acid (IX), m.p. 145–146°.

Anal. Calcd. for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.80; H, 7.51.

A glacial acetic acid solution of IX readily decolorized a solution of bromine in carbon tetrachloride, and an aqueous solution of IX liberated carbon dioxide from sodium bicarbonate solution.

Simultaneous dehydrogenation and decarboxylation of 0.2 g. of the adduct IX in the presence of 0.1 g. of 5% palladium-on-charcoal and 0.06 g. of copper-chromite catalyst was conducted over a period of 3 hours at a temperature of 300–320°. The crude material which collected on the cold finger of the dehydrogenation apparatus was purified by sublimation to produce 0.1 g. of anthracene, m.p. 215–217°. The mixed melting point obtained with a sample of authentic anthracene was 215–216°. Treatment of the anthracene obtained from the reaction with picric acid produced anthracene picrate, m.p. 136–137° (reported¹² m.p. 138°).

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(11) A. A. Pavlic and H. Adkins, *THIS JOURNAL*, **68**, 1471 (1946).