[Contribution from the Department of Chemistry, Wayne University]

Cyclic Dienes. I. 1,2-Dimethylenecyclohexane[1]

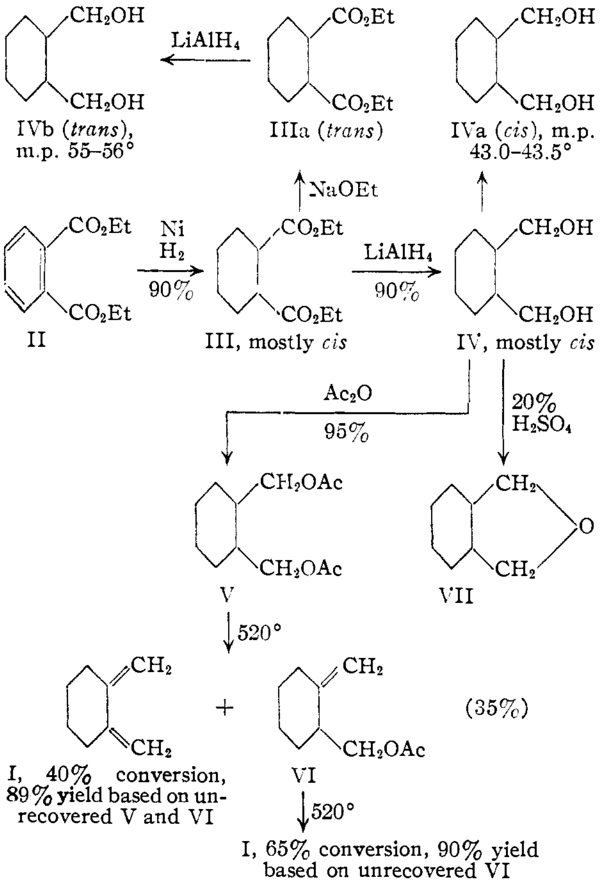
By William J. Bailey[2] and Harold R. Golden[3]

Received May 23, 1953

The cyclic diene, 1,2-dimethylenecyclohexane (I), was prepared in a four-step synthesis from diethyl phthalate in an over-all yield of 77%. The optimum conditions for the pyrolysis of a diester in the crucial step in the synthesis are described in detail. The structure of the diene was proved by ultraviolet absorption, ozonolysis, and conversion through a Diels–Alder adduct to the known β-naphthoic acid.

Cyclic dienes, such as cyclopentadiene, have attracted attention because they produce multicyclic Diels–Alder adducts, while 2,3-dialkylbutadienes have attracted attention because they produce high molecular weight polymers when treated with a free radical catalyst. The simple diene, 1,2-dimethylenecyclohexane (I), is of interest since it combines the characteristics of both these groups. Thus I would be expected to produce a high molecular weight, all-*cis* diene polymer in a free radical polymerization, and produce multicyclic Diels–Alder adducts that could be used in the synthesis of linear condensed polynuclear aromatic hydrocarbons and cyclodecane derivatives.

Diagram I



Since it is well recognized that unsaturation exocyclic to a six-membered ring has a strong tendency to rearrange to an internal position,[4] a method of synthesis was chosen that did not permit migration of one or both of the double bonds. Of the possible procedures that minimize rearrangements during the synthesis of olefins,[5] the pyrolysis of an ester was selected because of its simplicity. Thus a four-step synthesis for I was developed in an over-all yield of 77% starting with the readily available diethyl phthalate (II). II was hydrogenated with Raney nickel at high pressure to a mixture of *cis*- and *trans*-diethyl hexahydrophthalate (III).[6]

III was reduced with LiAlH$_4$ in high yields to the hexahydrophthalyl alcohol (IV). A satisfactory method for working up the reaction product was acidification with 10% hydrochloric acid followed by exhaustive extraction with ether. In a run in which 20% sulfuric acid was used, a 95% yield of the cyclic ether V resulted. IV was a mixture of isomers consisting of mostly the *cis* modification from which the pure *cis* form or low melting form, m.p. 43–45°, could be crystallized. The *trans* modification, or high melting form of hexahydrophthalyl alcohol (IVb), m.p. 55–56°, that has been reported by Adkins,[7] was prepared by first isomerizing III to the pure *trans* form IIIa with NaOEt before reduction with LiAlH$_4$. The hexahydrophthalyl diacetate (V), obtained by refluxing IV with acetic anhydride, was cracked at 510–520° through a 300 by 25-mm., helix-packed column to a mixture consisting of 40 mole % of I, 35 mole % of the olefin acetate VI and 20% unchanged V. The yield of the cyclic diene I based on unrecovered V and VI was 89%. VI can be pyrolyzed to I under approximately the same conditions in 90% yields based on unrecovered VI.

The pyrolysis was studied in detail in order to determine the optimum conditions. It was found that if a temperature and contact time were picked so that only 65% of the theoretical acetic acid was cracked out, the highest yield of pure diene was obtained. If more vigorous conditions, such as a higher temperature, were used, the helices became coated with carbon which catalyzed aromatization and rearrangement of the product and starting material. Thus even if more acetic acid was cracked out the purity and yield of the diene based on unrecovered starting material was substantially lower. Conversely, if a lower temperature was

---

[1] Presented before the Division of Organic Chemistry of the American Chemical Society, Philadelphia, Pa., April, 1950.

[2] Department of Chemistry, University of Maryland, College Park, Md.

[3] Atomic Energy Commission Fellow, 1949–1950.

[4] S. F. Birch, G. A. R. Kon and W. S. G. P. Norris, *J. Chem. Soc.*, 1361 (1923).

[5] E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 121.

[6] C. C. Price and M. Schwarcz, This Journal, **62**, 2894 (1940).

[7] H. Adkins, B. Wojcik and L. W. Covert, *ibid.*, **55**, 1673 (1933).

used less acetic acid was cracked out, thus reducing the conversion.

The structure of 1,2-dimethylenecyclohexane (I) was proved by its ultraviolet absorption, ozonolysis and conversion through a Diels–Alder adduct to the known β-naphthoic acid. The maximum in its ultraviolet absorption spectra at 220 mμ clearly indicates the presence of a conjugated diene structure. This maximum is, however, at a lower wave length than would be predicted from Woodward's rules.[8]

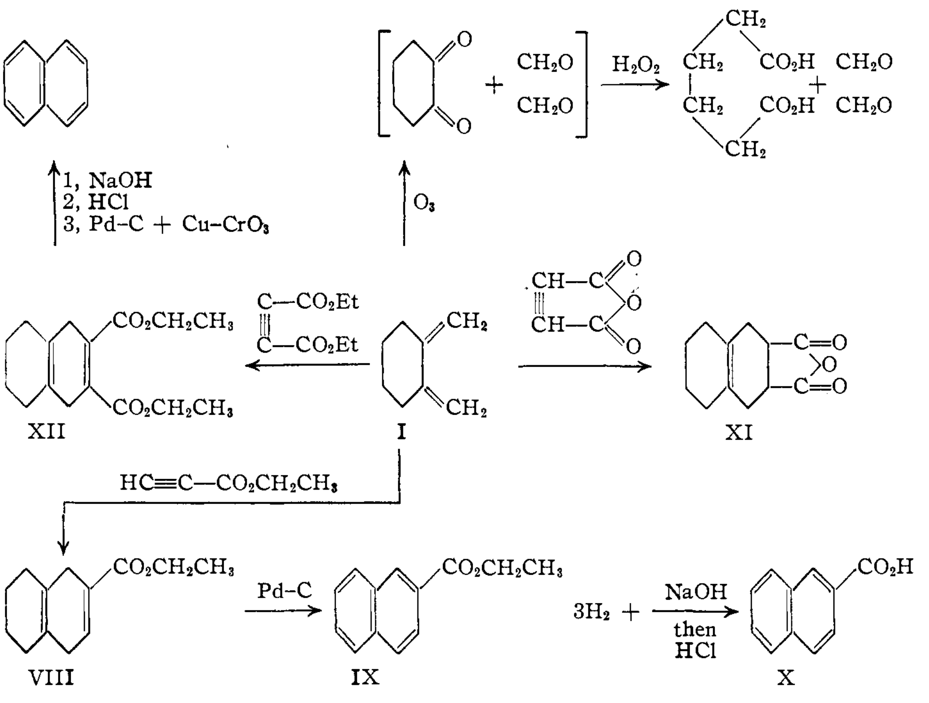
Ozonolysis of I followed by treatment with H_2O_2 produced a good yield of adipic acid plus formaldehyde. Schmid and Karrer[9] previously had obtained adipic acid from a somewhat similar diene.

The diene was further characterized by Diels–Alder products with maleic anhydride and ethyl propiolate.

The ethyl hexahydro-β-naphthoate (VIII) was dehydrogenated over Pd-on-C to produce the ethyl β-naphthoate (IX) plus the required volume of hydrogen. IX was then converted to the known crystalline β-naphthoic acid (X).

Reactions of this interesting diene will be reported later.

DIAGRAM II



Experimental

Diethyl Hexahydrophthalate (III).—Two hundred and twenty-eight grams (1 mole) of diethyl phthalate (Eastman Kodak Co.) was reduced with 20 g. (30 cc.) of Raney nickel catalyst at 1900 p.s.i. and 60°. The reduced product was distilled through an 18-in. glass-helices-packed column. The yield of diethyl hexahydrophthalate, b.p. 150–152° at 23 mm., $n^{25}\text{D}$ 1.4505, was 205 g. (90%).

***cis*-Hexahydrophthalyl Alcohol (VI).**—Fifty grams (1.3 moles) of $LiAlH_4$ was suspended in 1 liter of anhydrous ether in a 5-liter, 3-neck flask fitted with dropping funnel, Hershberg stirrer and condenser protected with a $CaCl_2$ tube. The suspension was stirred for 10 minutes until the larger pieces of $LiAlH_4$ were reduced in size. Two hundred and twenty-eight grams (1 mole) of diethyl hexahydrophthalate in 750 ml. of ether was added at such a rate as to produce gentle refluxing. By cooling the flask in ice, the addition could be effected in an hour. Fifteen minutes after the last addition, 50 ml. of water was added very cautiously with cooling to prevent the refluxing from becoming too vigorous during the exothermic decomposition of the excess hydride. Approximately 2 liters of 10% hydrochloric acid was then added with stirring until the aluminum hydroxide just dissolved and the solution was at *p*H 2. The ether layer was separated and the water layer extracted overnight with ether in an exhaustive extractor. The ether extracts were evaporated and the residue distilled under reduced pressure through a 10-in. helix-packed column. The yield of hexahydrophthalyl alcohol, b.p. 134–136° (3 mm.), was 128 g. (90%). On standing overnight, the distillate solidified to white crystals, m.p. 38–42°. Recrystallization from ether–hexane produced the pure *cis*-hexahydrophthalyl alcohol, m.p. 43–43.5°.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.73; H, 11.20. Found: C, 66.68; H, 11.24.

***trans*-Hexahydrophthalyl Alcohol (IVb).**—Ten grams of the original diethyl hexahydrophthalate (III) (presumably 75% *cis* and 25% *trans*) was isomerized to the pure diethyl *trans*-hexahydrophthalate (IIIa), b.p. 150° (22 mm.), $n^{25}\text{D}$ 1.4475, by refluxing with 100 ml. of 10% sodium ethoxide in ethyl alcohol. Seven and one-half grams (0.3 mole) of the *trans*-ester IIIa was reduced with 4.0 g. of $LiAlH_4$ in 200 ml. of ether. The crude glycol IVb, b.p. 120° (2 mm.), was worked up as described above. Recrystallization from ether–hexane produced the pure *trans*-hexahydrophthalyl alcohol, m.p. 55–56°.[10]

Hexahydrophthalyl Diacetate (V).—One hundred and seventy-five grams (1.2 moles) of hexahydrophthalyl alcohol and 1 ml. of pyridine were heated to 120° in a 1-liter, 3-neck flask fitted with dropping funnel and reflux condenser. Over a period of 30 minutes, 376 g. (3.6 moles) of acetic anhydride was added to the glycol. The acetic acid and anhydride were removed by vacuum distillation and the residue distilled under reduced pressure through an 8-in. column packed with $^1/_8$-in. glass helices. The yield of hexahydrophthalyl diacetate, b.p. 152–153° (10 mm.), $n^{25}\text{D}$ 1.4578, was 260 g. (95%).

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.21; H, 9.47. Found: C, 63.15; H, 9.61.

Pyrolysis of Hexahydrophthalyl Diacetate.—At a rate of 2 g. per minute, 456 g. (2.0 moles) of diacetate (V) was dropped into a 25-mm. Pyrex column externally heated to 515 ± 5° by a FD 303A Hoskins furnace and packed to a depth of 12 in. with $^1/_{16}$-in. Pyrex helices The addition was conducted in an inert atmosphere by introducing a slow stream of nitrogen at the top of the column. The pyrolysate was collected in a 1-liter flask cooled in a Dry Ice–acetone-bath. The pyrolysis products were washed free of acetic acid with distilled water, the washings were combined and an aliquot was titrated with standard NaOH. It was found in the optimum runs that 2.6 moles of AcOH or 65% of theoretical was cracked out. The washed material was dried over $MgSO_4$ and distilled (0.1 g. of *t*-butylcatechol added) under reduced pressure through a 10-in. column packed with $^1/_8$-in. glass helices. A typical run gave the following: fraction I, 86 g., b.p. 59–60° at 95 mm.; frac-

---

(8) R. B. Woodward, THIS JOURNAL, **63**, 1123 (1941).

(9) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **31**, 1067 (1948).

(10) This glycol is undoubtedly identical with the hexahydrophthalyl alcohol, m.p. 55–56°, reported by reference 7.

tion II, 6 g., b.p. 95–100° at 20 mm.; fraction III, 110 g., b.p. 100–108° at 20 mm.; fraction IV, 11 g., b.p. 145–152° at 10 mm.; fraction V, 80 g., b.p. 152–155° at 10 mm.; pot residue, 14 g.

It is assumed that fraction I was crude 1,2-dimethylenecyclohexane (I), 86 g. (40%), fractions II and III were crude 1-methylene-2-acetoxymethylcyclohexane (VI), 117 g. (35%), and fractions IV and V were recovered hexahydrophthalyl diacetate (V), 91 g. (20%). Fraction I was redistilled through a vacuum-jacketed 15-in. column packed with $^1/_{16}$-in. stainless steel helices using a total-condensation solenoid-controlled partial take-off to yield pure 1,2-dimethylenecyclohexane (I), b.p. 60–61° (90 mm.), 124° (740 mm.), n^{25}D 1.4718, λ_{max} 220 mμ, molecular extinction 10,050.

Anal. Calcd. for C_8H_{12}: C, 88.89; H, 11.11. Found: C, 88.80; H, 10.95.

Fractions II and III were redistilled through a 10-in. helices-packed column to give pure 1-methylene-2-acetoxymethylcyclohexane (VI), b.p. 105–106° (20 mm.), n^{25}D 1.4625.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.46; H, 9.54; neut. equiv., 168. Found: C, 71.68; H, 9.80; neut. equiv., 170.

Thus the yield of 1,2-dimethylenecyclohexane (I) based on unrecovered V and VI was 89%.

Pyrolysis of Olefin Acetate.—One hundred and ten grams (0.685 mole) of crude 1-methylene-2-acetoxymethylcyclohexane (fractions II and III above) was added to the heated column at 520°, as before, at the rate of 2 g. per minute. The pyrolysis products were worked up as previously described. Titration with base showed that 0.416 mole of AcOH (60.8%) was cracked out. A typical run was as follows: fraction I, 43 g., 59–60° at 95 mm.; fraction II, 2 g., 95–102° at 20 mm.; fraction III, 39 g., 102–105° at 20 mm.

Thus the yield of 1,2-dimethylenecyclohexane (fraction I) was 43 g. (58%) while 41 g. (37%) of the starting material was recovered. The yield of I based on unrecovered olefin acetate VI was 90%.

Proof of Structure of 1,2-Dimethylenecyclohexane

$\Delta^{9,(10)}$-Octahydronaphthalene-2,3-dicarboxylic Acid Anhydride (XI).—In a 100-ml., round-bottom flask fitted with a reflux condenser were placed 2.70 g. (0.025 mole) of the cyclic diene I, 2.45 g. (0.025 mole) of maleic anhydride and 50 ml. of ether. The solution spontaneously warmed up and a white crystalline solid crystallized out. After the mixture was refluxed for an additional 15 minutes, the ether was evaporated to produce 5.1 g. (99%) of crude adduct, m.p. 135–139°. Upon recrystallization from ether, pure $\Delta^{9,(10)}$-octahydronaphthalene-2,3-dicarboxylic acid anhydride (XI), m.p. 139–140°, was obtained.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 69.88; H, 6.83. Found: C, 69.80; H, 6.75.

Ethyl 1,4,5,6,7,8-Hexahydronaphthalene-2-carboxylate (VIII).—In a 100-ml. flask fitted with a reflux condenser were placed 5.4 g. (0.05 mole) of diene I, 4.9 g. (0.05 mole) of ethyl propiolate and 50 ml. of ether. After refluxing for 2 hours, the ether was evaporated and the residue was distilled under reduced pressure through a 6-in. helices-packed column to yield 7.8 g. (76%) of ethyl 1,4,5,6,7,8-hexahydronaphthalene-2-carboxylate (VIII), b.p. 130° (2 mm.), n^{25}D 1.4700.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.72; H, 8.73. Found: C, 75.61; H, 8.59.

β-Naphthoic Acid (X).—In a dehydrogenation apparatus[11] were placed 2.06 g. (0.01 mole) of the adduct VIII and 0.2 g. of 5% Pd-on-carbon. While heating for 2 hours at 300° in a stream of CO_2, 0.029 mole of hydrogen was collected. Upon distillation of the residue, 1.2 g. of ethyl β-naphthoate, b.p. 118–120° (2 mm.), n^{25}D 1.5942, was collected. Hydrolysis followed by recrystallization yielded β-naphthoic acid, m.p. 185°. Mixed melting point with an authentic sample showed no depression.

Diethyl 1,4,5,6,7,8-Hexahydronaphthalene-2,3-dicarboxylate (XII).—In 50 ml. of ether in a 100-ml. flask fitted with reflux condenser were dissolved 8.5 g. (0.05 mole) of diethyl acetylenedicarboxylate and 5.4 g. (0.05 mole) of diene I. The solution spontaneously warmed up and began to reflux. After heating for an additional 2 hours, the ether was evaporated off and the residue was vacuum-distilled through a 6-in. column packed with $^1/_8$-in. glass helices to yield 9.8 g. (71%) of the Diels–Alder adduct XII, b.p. 152–155° (1 mm.), n^{25}D 1.4990.

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.06; H, 7.91. Found: C, 68.92; H, 7.70.

Attempts to dehydrogenate this diester XI led to a mixture of products. However, hydrolysis followed by simultaneous decarboxylation and dehydrogenation with a mixture of 5% Pd-on-carbon and copper chromite in a dehydrogenation apparatus produced a crystalline sublimate on the cold finger. Recrystallization from alcohol produced naphthalene, m.p. 79°. Mixed melting point with an authentic sample showed no depression.

Ozonolysis of 1,2-Dimethylenecyclohexane (I).—In 75 ml. of ethyl acetate was dissolved 1.08 g. (0.01 mole) of the diene I and the solution cooled to −10°. After 0.019 mole of ozone was absorbed, the solution was evaporated to 5 ml. under reduced pressure at room temperature. To this residue was added 15 ml. of 30% H_2O_2 and 20 ml. of acetic acid and the mixture heated for 30 minutes on the steam-bath. The excess peroxide was destroyed and the solution was evaporated to dryness under reduced pressure to yield 1.25 g. of residue. Upon recrystallization from a small amount of water, 1.10 g. (75%) of adipic acid, m.p. 151–152°, was obtained. Mixed melting point with an authentic sample showed no depression. Formaldehyde liberated in the ozonolysis was identified as its dimethone derivative, m.p. 188–189°.

College Park, Maryland

---

[11] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1941, p. 462.