# Cyclic Dienes. XXII. Substituted 1,2-Dimethylene-4-cyclohexenes[1]

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Pyrolysis of 2,3-di-(acetoxymethyl)-$\Delta^{9(10)}$-octalin at 505° produced a 73% yield of 2,3-dimethylene-$\Delta^{9(10)}$-octalin, which is isomeric with the aromatic 6,7-dimethyltetralin. Similarly, the pyrolysis of 3,6-dimethyl-cis-Δ^4-tetrahydrophthalyl diacetate at the same temperature produced a 47% yield of 3,6-dimethyl-1,2-dimethylene-4-cyclohexene, isomeric with prehnitene. The structures of the trienes were proved by analyses, infrared and ultraviolet absorption spectra, conversions to solid Diels–Alder adducts, and isomerization to the corresponding aromatic derivatives. The isomerization of the 3,6-disubstituted triene was surprisingly slow.

Previous work has shown that the pyrolysis of esters is an excellent method for the synthesis of conjugated exocylic dienes.[5-11] In an effort to determine what other highly sensitive unsaturated compounds could be prepared by this pyrolytic method the syntheses of a series of highly unsaturated compounds and polyfunctional compounds were undertaken. For example, the pyrolysis of a triacetate gave the highly sensitive 2-vinylbutadiene[12] in good yields and the pyrolysis of a tetraacetate gave a good yield of 2,3-bis-(acetoxymethyl)-1,3-butadiene.[13] Further investigation has shown that during a vapor-phase pyrolysis in the absence of any charring there is little tendency for a double bond to rearrange. Thus the pyrolysis of hexahydroisophthalyl diacetate gives pure 1,3-dimethylenecyclohexane even though there is a strong driving force for one of the double bonds to rearrange from an exocyclic position to an endocyclic position into conjugation with the other double bond.[14] The synthesis of a series of isomers of aromatic compounds also was undertaken. The first compound in this series, 1,2-dimethylene-4-cyclohexene, isomeric with o-xylene, was prepared in a 92% yield by the pyrolysis of an unsaturated diacetate.[15] Spectroscopic evidence indicated that no o-xylene was present in the pyrolysate. This synthesis was extremely significant in view of the fact that the decomposition of the corresponding bis-quaternary ammonium hydroxide gives o-xylene as the only product.[16] The synthesis of isomers of aromatic compounds was then extended to the preparation of 4-methyl-1-2-dimethylene-4-cyclohexene, isomeric with pseudocumene, and 4,5-dimethyl-1,2-dimethylene-4-cyclohexene, isomeric with durene.[17]

It was of interest, therefore, to extend this study to a variety of other isomers of aromatic compounds containing a large number of substituents. For this reason the unsaturated diacetate, 2,3-di-(acetoxymethyl)-$\Delta^{9(10)}$-octalin (I),[8] was pyrolyzed at 505° under such conditions that only 57% of two molar equivalents of acetic acid was liberated. These conditions were selected in order to minimize any charring in the pyrolysis tube that could cause any rearrangement or aromatization. To
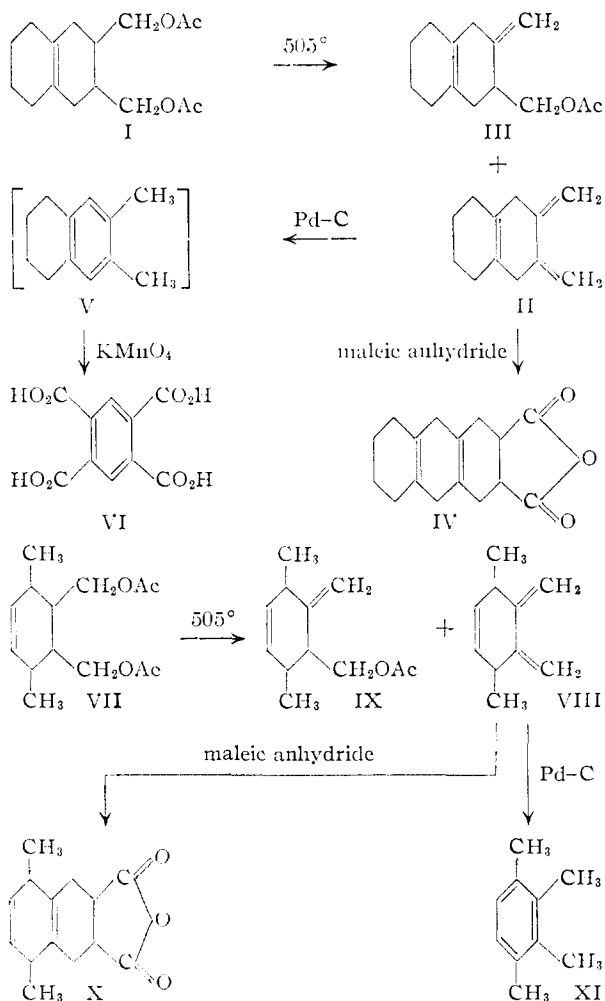
(1) Previous paper in this series, THIS JOURNAL, 79, 6516 (1957).

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(5) W. J. Bailey and H. R. Golden, THIS JOURNAL, 75, 4780 (1953).

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

(7) W. J. Bailey and W. R. Sorenson, ibid., 76, 5421 (1954).

(8) W. J. Bailey, C. W. Liao and G. H. Coleman, ibid., 77, 990 (1955).

(9) W. J. Bailey and R. L. Hudson, ibid., 78, 670 (1956).

(10) W. J. Bailey and W. B. Lawson, ibid., 77, 1606 (1955); 79, 1444 (1957).

(11) W. J. Bailey and W. A. Klein, ibid., 79, 3124 (1957).

(12) W. J. Bailey and J. Economy, ibid., 77, 1133 (1955).

(13) W. J. Bailey and W. R. Sorenson, ibid., 78, 2287 (1956).

(14) W. J. Bailey and J. Economy, J. Org. Chem., 23, in press (1957).

(15) W. J. Bailey and J. Rosenberg. THIS JOURNAL, 77, 73 (1955).

(16) J. R. Ladburg and E. E. Turner, J. Chem. Soc., 3885 (1954).

(17) W. J. Bailey, J. Rosenberg and L. J. Young, THIS JOURNAL, 77, 1163 (1955).

avoid carbonization the pyrolysis was carried out in an atmosphere of oxygen-free nitrogen. From the pyrolysate was obtained a 30% conversion to 2,3-dimethylene-$\Delta^{9(10)}$-octalin (II), isomeric with the aromatic 6,7-dimethyltetralin. At the same

time a 36% yield of the intermediate 2-methylene-3-acetoxymethyl-$\Delta^{9(10)}$-octalin (III) and a 23% recovery of unchanged starting material I were obtained. The yield of the triene II, based on unrecovered I and III, was, therefore, 73%.

The structure of 2,3-dimethylene-$\Delta^{9(10)}$-octalin (II) was indicated by chemical as well as spectral evidence. The triene II reacted with maleic anhydride to give the solid $\Delta^{4a(10a),5a(9a)}$-decahydroanthracene-2,3-dicarboxylic anhydride (IV) in a 50% yield. Treatment of the triene II with palladium-on-carbon catalyst for 30 hours promoted isomerization to the intermediate 6,7-dimethyltetralin (V), which was not isolated but was oxidized directly to pyromellitic acid (VI) with potassium permanganate in a 34% over-all yield. The presence of a pair of conjugated double bonds exocyclic to a six-membered ring was indicated by the fact that there was no maximum or minimum in the ultraviolet spectrum above 220 mμ, but the ϵ was rapidly increasing as the wave length was lowered and appeared to reach a maximum just below 220 mμ. (For comparison, 1,2-dimethylenecyclohexane possesses a maximum in its spectrum at 220 mμ.) The infrared absorption spectrum exhibited strong bands at 2970, 1645, 1510, 1460, 1445, 1244, 1230, 1190, 1012, 895, 880, 825 and 665 cm.$^{-1}$ and medium bands at 1840, 1655, 1615, 1375, 1352, 1290, 1095, 1070, 1035, 990, 975, 950 and 910 cm.$^{-1}$.

In a similar fashion the unsaturated diacetate, 3,6-dimethyl-Δ^4-tetrahydrophthalyl diacetate (VII),[18] was pyrolyzed at 505° under such conditions that only 53% of two molar equivalents of acetic acid was liberated. Under these conditions only a slight amount of carbonization that might cause rearrangement occurred. From the pyrolysis was obtained a 26% conversion to 3,6-dimethyl-1,2-dimethylene-4-cyclohexene (VIII), which is isomeric with prehnitene (XI). At the same time there were obtained a 27% yield of the intermediate 3,6-dimethyl-1-methylene-2-acetoxymethyl-4-cyclohexene (IX) plus an 18% recovery of unchanged starting ester VII. The yield of the triene VIII, based on unrecovered VII and IX, was 47%.

The structure of 3,6-dimethyl-1,2-dimethylene-4-cyclohexene (VIII) was proved in a manner similar to that used for II. Maleic anhydride plus the triene VIII formed the solid derivative, 5,8-dimethyl - $\Delta^{6,9(10)}$ - hexahydronaphthalene - 2,3-dicarboxylic anhydride (X). When the triene VIII was heated under reflux for 48 hours with a palladium-on-carbon catalyst, only part of it was isomerized to prehnitene (XI). The prehnitene (XI) was identified by conversion to a known solid sulfonamide and by determination of its infrared spectrum. The material from the isomerization had a spectrum very similar to that of prehnitene (XI)[19] plus several weak peaks from the triene VIII. It is noteworthy that, in contrast to the isomerization of the parent 1,2-dimethylene-4-cyclohexene,[15] the isomerization of the 3,6-dimethyl-1,2-dimethylene-4-cyclohexene (VIII) is neither fast nor complete.

Apparently, in spite of the fact that the triene VIII is being converted to an aromatic structure the reaction is slow. One can speculate that the steric interaction of the four methyl groups being forced into one plane partially counteracts the usual driving force for aromatization. In other words the non-planar triene VIII is somewhat stabilized by steric hindrance.

As noted, the presence of a pair of conjugated bonds exocyclic to a six-membered ring in VIII was indicated by the fact that the ultraviolet spectrum of VIII did not possess a maximum or minimum above 220 mμ but the ϵ was increasing rapidly as the wave length was lowered and appeared to reach a maximum just below 220 mμ. The structure of VIII also was confirmed by its infrared absorption spectrum which had strong bands at 2970, 1740, 1570, 1450, 1355, 1245, 1220, 1070, 1050, 1028, 990, 950, 895 and 800–850 cm.$^{-1}$ and medium bands at 1280, 1190 and 1095 cm.$^{-1}$.

It can be concluded that the pyrolysis of esters is an excellent procedure for the synthesis of unstable unsaturated compounds. It also appears that the tendency for some isomers of aromatic compounds to aromatize is not as great as previously supposed. These facts should make possible the synthesis of many other types of isomers of aromatic compounds.

Experimental[20]

2,3-Dimethylene-$\Delta^{9(10)}$-octalin (II).—At the rate of 1.3 g. per minute, 141 g. (0.51 mole) of 2,3-di-(acetoxymethyl)-$\Delta^{9(10)}$-octalin (I)[8] was dropped through a vertical Vycor tube packed with $^1/_{16}$-inch Pyrex helices and externally heated at 505° by a Hoskins FD 303A electric furnace as previously described.[21] In order to minimize charring, a stream of oxygen-free nitrogen was continuously passed through the apparatus during the pyrolysis. The pyrolysate, which was condensed in a 6-inch coil condenser and collected in a side-inlet flask cooled in a Dry Ice–acetone-bath, was diluted with 50 ml. of ether. The ether solution was extracted with five 100-ml. portions of water until free of acetic acid and then dried over anhydrous sodium carbonate. (Titration of an aliquot portion of the aqueous extracts indicated that 57% of two molar equivalents of acetic acid had been liberated.) After the ether had been removed by evaporation under reduced pressure, the residue was distilled through a 12-inch, helix-packed column to yield 25 g. (30%) of 2,3-dimethylene-$\Delta^{9(10)}$-octalin (II), b.p. 165° (70 mm.), n^{25}D 1.5280, d^{24}_4 0.9614; 40 g. (36%) of 2-methylene-3-acetoxymethyl-$\Delta^{9(10)}$-octalin (III); and 32 g. (23% recovery) of unchanged starting diester I. The yield of triene II, based on unrecovered I and III, was 73%.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.91; H, 10.24.

$\Delta^{4a(10a),5a(9a)}$-**Decahydroanthracene-2,3-dicarboxylic Anhydride (IV).** A mixture of 2.1 g. (0.013 mole) of 2,3-dimethylene-$\Delta^{9(10)}$-octalin (II) and 1.28 g. (0.013 mole) of maleic anhydride in 20 ml. of ether was heated under reflux for 3 days. After the mixture was allowed to cool, the precipitate which formed was removed by filtration. Recrystallization from acetone–petroleum ether (30–60°) gave 1.7 g. (50%) of $\Delta^{4a(10a),5a(9a)}$-decahydroanthracene-2,3-dicarboxylic anhydride (IV), m.p. 245° dec.

(18) W. J. Bailey and R. L. Hudson, THIS JOURNAL, **78**, 2806 (1956).

(19) P. J. Launer and D. A. McCauley, *Anal. Chem.*, **23**, 1875 (1951).

(20) The authors are grateful to Dr. Mary Aldridge, Kathryn Gerdeman and Vivian Kapuscinski for the microanalyses and to Kathryn Gerdeman and Dr. Joseph Wenograd for the infrared absorption spectra. The infrared spectra were determined on the pure liquid VIII with a sodium chloride prism in a Perkin–Elmer model 12-C infrared spectrometer modified for double-pass operation and on a carbon tetrachloride solution of II in a Baird Associates double-beam infrared spectrometer. The ultraviolet absorption spectra were determined in purified cyclohexane with a Beckman DU spectrophotometer. All melting points are corrected.

(21) W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956).

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.43; H, 7.02. Found: C, 74.20; H, 7.34.

Isomerization of 2,3-Dimethylene-$\Delta^{9(10)}$-octalin (II).—A mixture of 2.0 g. of 2,3-dimethylene-$\Delta^{9(10)}$-octalin (II) and 0.5 g. of palladium-on-carbon catalyst was heated under reflux for 30 hours. After the catalyst had been removed by filtration, the filtrate was oxidized with an excess of potassium permanganate according to the method of Coulson.[22] Ethyl alcohol was added to the hot solution in order to decompose the excess potassium permanganate. The solution was then acidified and extracted with ether in an exhaustive ether extractor. Evaporation of the ether produced a solid residue which was recrystallized from an acetone–benzene mixture to yield 1.1 g. (34%) of pyromellitic acid (VI), m.p. 260–264° dec. (reported[22] m.p. 260–264° dec.).

3,6-Dimethyl-1,2-dimethylene-4-cyclohexene (VIII).—At the rate of 1.5 g. per minute, 105 g. (0.413 mole) of 3,6-dimethyl-*cis*-Δ^4-tetrahydrophthalyl diacetate (VII) was dropped through the vertical Vycor pyrolysis tube heated at 505° as described above. Because of the tendency of this compound to char the pyrolysis was interrupted at the midpoint and a clean pyrolysis tube was inserted in the apparatus. During the pyrolysis and before addition of the ester to either pyrolysis tube, a slow stream of oxygen-free nitrogen was introduced at the top of the apparatus. The pyrolysate was dissolved in 100 ml. of ether and the solution was extracted several times with distilled water. (Titration of an aliquot of the aqueous extracts indicated that 53% of two molar equivalents of acetic acid had been eliminated.) After the ether solution had been dried over anhydrous magnesium sulfate, the ether was removed by distillation under reduced pressure. The residue was fractionated through a 6-inch, helix-packed column to yield 14.3 g. (26%) of 3,6-dimethyl-1,2-dimethylene-4-cyclohexene (VIII), b.p. 49° (15 mm.), n^{25}D 1.4884; 21.6 g. (27%) of 3,6-dimethyl-1-methylene-2-acetoxymethyl-4-cyclohexene (IX), b.p. 76° (1.5 mm.), n^{25}D 1.4762; and 19 g. (18% recovery) of the starting diester VII. The yield of the triene VIII, based on unrecovered VII and IX, was 47%.

(22) E. A. Coulson, *J. Chem. Soc.*, 1305 (1938).

Anal. Calcd. for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.79; H, 10.22. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34:. Found: C, 74.26; H, 9.31.

5,8-Dimethyl-$\Delta^{6,9(10)}$-hexahydronaphthalene-2,3-dicarboxylic Anhydride (X).—A mixture of 1.96 g. (0.02 mole) of maleic anhydride plus 2.68 g. (0.02 mole) of 3,6-dimethyl-1,2-dimethylene-4-cyclohexene (VIII) in 50 ml. of ether was heated under reflux for 21 hours. After about half of the ether had been removed by evaporation, the concentrated solution was cooled to form a precipitate. The solid was removed by filtration and recrystallized from a chloroform–petroleum ether mixture to yield 1.1 g. (24%) of 5,8-dimethyl-$\Delta^{6,9(10)}$-hexahydronaphthalene-2,3-dicarboxylic anhydride (X), m.p. 162–163°. Further evaporation of the ether filtrate gave a yellow oil that could not be crystallized.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.14; H, 6.84.

Isomerization of 3,6-Dimethyl-1,2-dimethylene-4-cyclohexene (VIII) to Prehnitene (XI).—A mixture of 7.6 g. (0.057 mole) of 3,6-dimethyl-1,2-dimethylene-4-cyclohexene (VIII) and 0.2 g. of a 10% palladium-on-carbon catalyst was heated under reflux for 48 hours. The catalyst was removed by filtration and the filtrate was fractionated through a 6-inch, helix-packed column to yield 2.9 g. of a mixture (presumably triene VIII and prehnitene), b.p. 50–68° (20 mm.), n^{25}D 1.4938, and 2.6 g. of slightly impure prehnitene (XI), b.p. 42–45° (0.9 mm.), n^{25}D 1.5020–1.5072 (reported b.p. 75–75.5° (6.5 mm.)[23], n^{25}D 1.5187[24]).

By the procedure of Huntress and Autenrieth,[25] 1.0 g. of the impure prehnitene (XI) was converted to 2,3,4,5-tetramethylbenzenesulfonamide, m.p. 179–181° (reported[25] m.p. 183.5–184°), with chlorosulfonic acid.

(23) L. I. Smith with F. H. MacDougall, THIS JOURNAL, **51**, 3005 (1929).

(24) K. v. Auwers, *Ber.*, **55**, 26 (1922).

(25) E. H. Huntress and J. S. Autenrieth, THIS JOURNAL, **63**, 3446 (1941).

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Polynuclear Aromatic Hydrocarbons. IX.[1] The Synthesis of 3,4-Benzpyrene and 7-Methyl-3,4-benzpyrene

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The synthesis of 3,4-benzpyrene (X) and 7-methyl-3,4-benzpyrene (XI) from 5-keto-5,6,6a,7,8,9,10,10a-octahydrochrysene (I) is described. The ketone I was converted by the Reformatsky reaction to a mixture of the two unsaturated acids III and IV which were reduced and cyclized to the corresponding ketones VII and VIII. When either VII or VIII was reduced and dehydrogenated, 3,4-benzpyrene (X) was obtained. Treatment of VII with methylmagnesium iodide followed by dehydrogenation afforded 7-methyl-3,4-benzpyrene (XI), one of the two monomethyl-3,4-benzpyrenes whose synthesis has yet to be described. The attempted preparation of X by the cyclodehydrogenation of XII and XIII afforded chrysene by the ejection of an ethyl group.

In a recent communication[4] we reported the preparation of the ketoöctahydrochrysene (I) from naphthalene and *trans*-2-hydroxy-cyclohexaneacetic acid lactone. It became apparent that this ketone (I) could serve not only as a useful precursor to the chrysene ring system but also to the important 3,4-benzpyrene (X) nucleus.[5] Moreover, the synthetic scheme whereby we planned to elaborate X from I also seemed applicable to the preparation of 7-methyl-3,4-benzpyrene (XI), a hydrocarbon of considerable interest for biological

(1) Paper VIII, D. D. Phillips and T. B. Hill, THIS JOURNAL, **80**, 3663 (1958).

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(4) D. D. Phillips and D. N. Chatterjee, THIS JOURNAL, **80**, 1360 (1958).

(5) These numbering systems are employed throughout this paper:

chrysene   3,4-benzpyrene