Twenty-four grams (0.15 mole) of bromine was added over a period of 2 hr. to 25 g. (0.149 mole) of 1,1,1,3,3-pentafluoro-2-chloropropene[42] in a flask provided with mechanical stirrer, dropping funnel and a Dry Ice–acetone cooled condenser. The reaction proceeded rapidly and exothermically as soon as ultraviolet light was applied. After washing with aqueous sodium bisulfite and drying, 27 g. (82%) of XIX was obtained, b.p. 104°, or 46° (71 mm.).

Anal. Calcd. for $C_3F_5Br_2Cl$: Cl, 10.86. Found: Cl, 10.81.

RARITAN, N. J.

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[42] A. L. Henne, A. M. Whaley and J. K. Stevenson, THIS JOURNAL, **63**, 3478 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Cyclic Dienes. XVII. 3-Methylenecyclohexene[1,2]

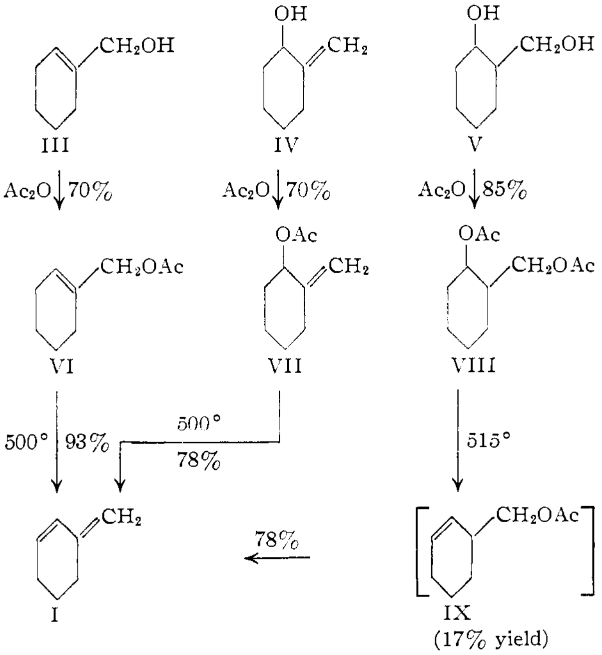
BY WILLIAM J. BAILEY AND JOHN C. GOOSSENS[3]

RECEIVED NOVEMBER 14, 1955

3-Methylenecyclohexene was prepared in three steps from 2-hydroxymethylenecyclohexanone in an over-all yield of 42%. In the final step the pyrolysis of each of three esters, 1-cyclohexenylmethyl acetate, 2-methylenecyclohexyl acetate and 2-acetoxymethylcyclohexyl acetate, produced the diene in 78 to 95% yields. The structure of the 3-methylenecyclohexene was proved by analysis, infrared and ultraviolet absorption spectra and ozonolysis to known derivatives.

In a research program designed to correlate the structure and properties of hydrocarbon polymers, an all-*cis* diene polymer related to natural rubber was prepared.[4] In contrast to natural rubber, poly-1,2-dimethylenecyclohexane was a high melting crystalline solid. Since the structure of balata (or gutta percha) differs from that of natural rubber only in the configuration around the double bonds,[5] the high melting point of balata has been attributed to its all-*trans* configuration. It was of interest, therefore, to prepare a synthetic all-*trans* diene polymer related in structure to balata. The all-*cis* polymer was prepared by the synthesis and polymerization of a diene in which the 2- and 3-positions were connected through a six-membered ring.[6] In this polymer the six-membered ring containing the double bond must have the *cis* configuration and at every monomer unit the polymer chain must, as a consequence, enter and leave from the same side of the double bond. It was reasoned, therefore, that a diene with a six-membered ring connecting the 1- and 3-positions should produce an all-*trans* polymer. Thus the ring would restrict one end of the polymer chain and the substituent in the 3-position to the *cis* configuration, so that at every monomer unit the polymer chain must enter and leave from opposite sides of the double bond. The simplest diene that has a six-membered ring connecting the 1- and 3-positions is 3-methylenecyclohexene (I).

3-Methylenecyclohexene (I) was synthesized from 2-hydroxymethylenecyclohexanone (II) in three steps in an over-all yield of 42%. By a modification of the procedure of Dreiding and Hartman,[7] 2-hydroxymethylenecyclohexanone (II) was reduced by the reflux of an ether solution with lithium aluminum hydride for 24 hr. to produce a mixture of an 11% yield of 1-cyclohexenylmethanol (III), a 34% yield of 2-methylenecyclohexanol (IV) and a 21% yield of 2-hydroxymethylcyclohexanol (V). The unsaturated alcohols III and IV were acetylated with acetic anhydride to produce 70% yields of 1-cyclohexenylmethyl acetate (VI) and 2-methylenecyclohexyl acetate (VII), respectively. The saturated diol V was converted with acetic anhydride to 2-acetoxymethylcyclohexyl acetate (VIII) in an 85% yield. The acetate VI[8] previously had been prepared in a low yield by the reaction of cyclohexene and formaldehyde in the presence of acetic anhydride, while VII[9] was prepared in an unreported yield by the oxidation of methylenecyclohexane with selenium dioxide in acetic acid. VIII[10] had been prepared from V in an unreported yield. The three acetates VI, VII and VIII previously were characterized only by their boiling points.



3-Methylenecyclohexene (I) was prepared by

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[1] Previous paper in this series, THIS JOURNAL, **78**, 670 (1956).

[2] Presented before the Division of Polymer Chemistry at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March, 1955.

[3] Office of Naval Research Fellow, 1951–1954.

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

[5] K. H. Meyer, "High Polymers. IV. Natural and Synthetic High Polymers," Interscience Publishers, Inc., New York, N. Y., 1950.

[6] W. J. Bailey and H. R. Golden, THIS JOURNAL, **75**, 4780 (1953).

[7] A. S. Dreiding and J. A. Hartman, *ibid.*, **75**, 939 (1953).

[8] S. Olsen, *Ber.*, **81**, 131 (1948).

[9] M. Mousseron, R. Jacquier and F. Wintermitz, *Compt. rend.*, **224**, 1230 (1947).

[10] H. Rupe and O. Klemm, *Helv. Chim. Acta*, **21**, 1538 (1938).

three different routes, all involving the pyrolysis of esters. The unsaturated acetate VI was pyrolyzed by the addition of the liquid VI to a helix-packed column heated at 500°. It previously was found that, if charring was avoided during the pyrolysis of esters, isomers of aromatic compounds, such as 1,2-dimethylene-4-cyclohexene, could be prepared in high yields.[11] Therefore, extreme care was taken to avoid charring by conduction of the pyrolysis in an inert atmosphere. However, since VI was a monoacetate, it was possible to eliminate over 90% of the theoretical amount of acetic acid without any charring. Under these conditions, 3-methylenecyclohexene (I) was obtained in a 93% yield and no attempt was made to recover any starting material. The mechanism of elimination of the acetic acid from VI must be more complex than for simple esters.[12] The study of molecular models showed that a quasi eight-membered ring involving the allylic hydrogen was not highly probable. This, in a sense, is an extension of Bredt's rule in which a cyclic reaction intermediate that involves a double bond at a bridgehead carbon atom would require a high energy of activation. One must conclude that VI undergoes an allylic rearrangement similar to the initial step in the Claisen rearrangement of phenyl allyl ethers to form 2-methylenecyclohexyl acetate (VII), which then eliminates acetic acid by the conventional mechanism to form the diene I. When VII was pyrolyzed under the same conditions that were used for the pyrolysis of the isomeric VI, a 78% yield of 3-methylenecyclohexene (I) was obtained.

When the diacetate VIII was pyrolyzed at 515°, it was possible to eliminate only 87% of two molar equivalents of acetic acid and still prevent charring. Under these conditions, a 78% conversion to the diene I was obtained. At the same time, a 17% yield of the intermediate olefin acetate IX was obtained so that the total yield of I and IX was 95%. The structure of the olefin acetate IX, as expected on the basis of previous work on the pyrolysis of esters, was 3-cyclohexenylmethyl acetate. The secondary acetoxy group would be eliminated more easily than the primary group,[13] and the direction of elimination would be away from the tertiary hydrogen.[14] For example, it was shown previously that pyrolysis of *cis*- or *trans*-2-methylcyclohexyl acetate gave almost exclusively 3-methylcyclohexene.[15]

The structure of IX was confirmed by its infrared absorption spectrum, which showed strong bands at 1030 and 1230 cm.$^{-1}$ and medium intensity bands at 975, 1360, 1725 and 2860 cm.$^{-1}$. The spectrum of the isomer VI showed strong bands at 920, 955, 970, 1020 and 1230 cm.$^{-1}$ and medium bands at 795, 825, 1130, 1170, 1360, 1750 and 2860 cm.$^{-1}$ and that of VII showed strong bands at 895, 910, 950, 995, 1050 and 1230 cm.$^{-1}$ and medium bands at 935, 1090, 1120, 1325, 1740 and 2860 cm.$^{-1}$.

The structure of 3-methylenecyclohexene (I) was proved by analysis, infrared and ultraviolet absorption spectra and ozonolysis to known derivatives. The ultraviolet absorption spectrum in cyclohexane showed a maximum ϵ of 21,000 at 231 mμ, indicating a pair of conjugated double bonds with two substituents and one exocyclic double bond.[16] This structure also was confirmed by the infrared absorption spectrum which possessed strong bands at 770, 875 and 910 cm.$^{-1}$ and medium bands at 960, 980, 990, 1050, 1120, 1220, 1250, 1330, 1380, 1430, 1700 and 2800 cm.$^{-1}$. Ozonization of 3-methylenecyclohexene (I) produced formaldehyde, which was identified as its methone derivative. Oxidative cleavage of the ozonide produced a 67% yield of the solid glutaric acid.

The polymerization of this interesting diene will be reported separately.

Experimental[17]

1-Cyclohexenylmethyl Acetate (VI).—After a mixture of 72 g. (0.63 mole) of 1-cyclohexenylmethanol (III), b.p. 98–99° (27 mm.), $n^{25}\mathrm{D}$ 1.4868 (reported[7] b.p. 98–99° (27 mm.), $n^{25}\mathrm{D}$ 1.4905), 10 g. of acetic acid and 400 g. (3.9 moles) of acetic anhydride had been heated under reflux for 3 days, the excess acetic anhydride and acetic acid were removed by distillation at atmospheric pressure. The residue was fractionated through a 12-inch, helix-packed column to yield 68 g. (70%) of 1-cyclohexenylmethyl acetate (VI), b.p. 96–97° (18 mm.), $n^{25}\mathrm{D}$ 1.4619 (reported[8] b.p. 82° (12 mm.)).

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.91; H, 8.93.

2-Methylenecyclohexyl Acetate (VII).—After a mixture of 223 g. (1.95 moles) of 2-methylenecyclohexanol (IV), b.p. 83–84° (26 mm.), $n^{25}\mathrm{D}$ 1.4848 (reported[7] b.p. 82–85° (27 mm.), $n^{25}\mathrm{D}$ 1.4880), 30 g. of acetic acid and 700 g. (6.9 moles) of acetic anhydride had been heated under reflux for 3 days, the excess acetic anhydride and acetic acid were removed by distillation. The residue was fractionated through a 12-inch, helix-packed column to produce 210 g. (70%) of 2-methylenecyclohexyl acetate (VII), b.p. 83–84° (20 mm.), $n^{25}\mathrm{D}$ 1.4552 (reported[9] b.p. 85° (15 mm.)).

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.40; H, 9.26.

2-Acetoxymethylcyclohexyl Acetate (VIII).—After a mixture of 190 g. (1.44 moles) of 2-hydroxymethylcyclohexanol (V), b.p. 116–118° (5.5 mm.), $n^{25}\mathrm{D}$ 1.4900 (reported[7] b.p. 148–152° (24 mm.), $n^{25}\mathrm{D}$ 1.4920), 40 g. of acetic acid and 900 g. (8.8 moles) of acetic anhydride had been heated under reflux for 2 days, the excess acetic anhydride and acetic acid were removed by distillation through a 12-inch, helix-packed column. The residue was fractionated through the same column to yield 265 g. (85%) of 2-acetoxymethylcyclohexyl acetate (VIII), b.p. 109–110° (5 mm.), $n^{25}\mathrm{D}$ 1.4495 (reported[10] b.p. 133° (13 mm.)).

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.67; H, 8.47. Found: C, 61.95; H, 8.58.

3-Methylenecyclohexene (I). A. By Pyrolysis of 1-Cyclohexenylmethyl Acetate (VI).—Through a 25-mm. Vycor tube packed to a depth of 12 inches with $^1/_8$-inch Pyrex helices and externally heated at 500° with an FD 303A Hoskins electric furnace was dropped 51 g. (0.33 mole) of 1-cyclohexenylmethyl acetate (VI) at a rate of 0.5 g. per minute. The system was continuously flushed with a slow stream of dry, oxygen-free nitrogen. The pyrolysate was condensed in a 6-inch spiral condenser and collected in a 100-ml., side-inlet flask that was immersed in a Dry Ice–acetone-bath. The pyrolysate was washed with water until it was free of acetic acid and then dried over potassium carbonate. (Titration of an aliquot of the aqueous washings indicated

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[11] W. J. Bailey and J. Rosenberg, THIS JOURNAL, **77**, 73 (1955); W. J. Bailey, J. Rosenberg and L. J. Young, *ibid.*, **77**, 1163 (1955).

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

[13] W. J. Bailey, J. J. Hewitt and C. King, THIS JOURNAL, **77**, 357 (1955).

[14] W. J. Bailey and C. King, *ibid.*, **77**, 75 (1955).

[15] W. J. Bailey and L. Nicholas, *J. Org. Chem.*, **21**, in press (1956).

[16] R. B. Woodward, THIS JOURNAL, **63**, 1123 (1941); **64**, 76 (1942).

[17] The authors are grateful to Dr. Mary Aldridge and Kathryn Gerdeman for the analyses and to Joseph Wenograd and Kathryn Gerdeman for the infrared absorption spectra. The ultraviolet spectrum was determined in cyclohexane with a Beckman DU spectrophotometer and the infrared absorption spectra were determined with the pure liquids in a Perkin–Elmer model 12-C spectrophotometer modified for double-pass operation.

that 95% of the theoretical amount of acetic acid had been liberated.) Distillation of the dried organic layer through a 12-inch, helix-packed column produced 28.5 g. (93%) of 3-methylenecyclohexene (I), b.p. 109°, $n^{25}D$ 1.4897.

Anal. Calcd. for C_7H_{10}: C, 89.29; H, 10.71. Found: C, 89.46; H, 10.67.

B. **By Pyrolysis of 2-Methylenecyclohexyl Acetate (VII).**—By the use of the apparatus described above, 57 g. (0.37 mole) of 2-methylenecyclohexyl acetate (VII) was pyrolyzed at 500° at the rate of 0.5 g. per minute. The pyrolysate was washed, dried and distilled through a 12-inch, helix-packed column, as described, to yield 27 g. (78%) of 3-methylenecyclohexene (I), b.p. 109°, $n^{25}D$ 1.4894. (Titration of an aliquot of the aqueous washings indicated that 95% of the theoretical amount of acetic acid had been liberated.)

C. **By Pyrolysis of 2-Acetoxymethylcyclohexyl Acetate (VIII).**—Pyrolysis of 95 g. (0.44 mole) of 2-acetoxymethyl-1-cyclohexyl acetate (VIII) was carried out at 515° over a 3.5-hr. period in the apparatus described above. The pyrolysate was washed, dried and distilled through a 12-inch, helix-packed column to yield 32.5 g. (78%) of 3-methylenecyclohexene (I), b.p. 109°, $n^{25}D$ 1.4898, and 12 g. (17%) of 3-cyclohexenylmethyl acetate (IX), b.p. 100–101° (25 mm.), $n^{25}D$ 1.4576. (Titration of an aliquot of the aqueous washings indicated that 87% of two molar equivalents of acetic acid had been liberated.)

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.13; H, 9.20.

Ozonolysis of 3-Methylenecyclohexene (I).—At the rate of 6 liters per hour, a stream of oxygen containing 0.7 millimole of ozone per liter was passed for 7 hr. through a solution of 1.7 g. (0.018 mole) of 3-methylenecyclohexene (I) in 100 ml. of ethyl acetate cooled in a Dry Ice-methyl Cellosolve-bath. The ethyl acetate solution was then concentrated to a volume of 10 ml. by evaporation of the solvent at room temperature under a pressure of 40 mm. A 1-ml. aliquot of this concentrate, mixed with 0.5 g. of zinc dust, was carefully added with stirring to 25 ml. of 1 *N* hydrochloric acid. This solution was filtered and the filtrate was mixed with an equal volume of a saturated aqueous solution of methone. Recrystallization of the resultant precipitate from cyclohexane yielded white needles of the methone derivative of formaldehyde, m.p. 189–190° (reported[18] m.p. 191–191.5°). The remaining concentrate was heated on a steam-bath with 15 ml. of 30% hydrogen peroxide solution until the mixture became homogeneous. After the mixture had been heated for an additional hour, the excess hydrogen peroxide was decomposed by vigorous agitation of the hot solution with a platinum wire for 5 hr. The solution was evaporated to dryness and the residue was recrystallized from benzene to yield 1.6 g. (67%) of glutaric acid, m.p. 95–96° (reported[19] m.p. 97°). A mixed melting point determination with an authentic sample of glutaric acid showed no depression.

(18) E. C. Horning and M. G. Horning, *J. Org. Chem.*, **11**, 95 (1946).

(19) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

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[Contribution from the Department of Chemistry, University of Maryland]

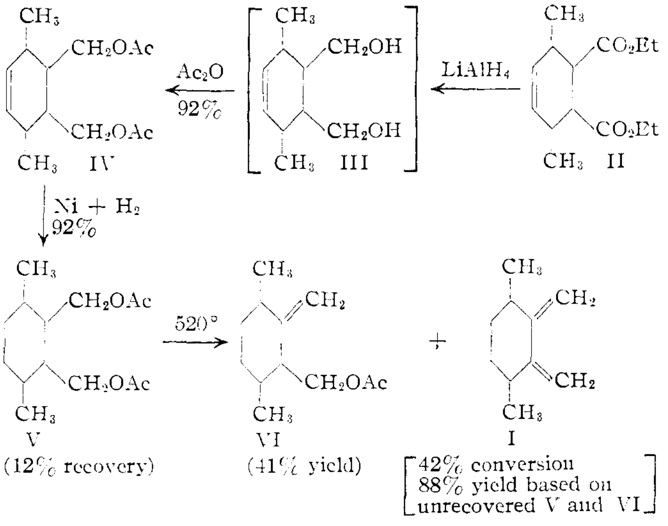
Cyclic Dienes. XVIII. 3,6-Dimethyl-1,2-dimethylenecyclohexane[1]

By William J. Bailey and Robert L. Hudson[2]

Received November 14, 1955

3,6-Dimethyl-1,2-dimethylenecyclohexane was synthesized in essentially four steps from 2,4-hexadiene in an over-all yield of 30%. In the final step a diacetate was pyrolyzed to produce the diene in an 88% yield, based on unrecovered material. The structure of the diene was proved by ultraviolet and infrared absorption spectra and conversion to a solid derivative through a Diels–Alder reaction.

Poly-1,2-dimethylenecyclohexane,[3] even though it is related in structure to natural rubber, possesses no rubbery properties at room temperature but is a white crystalline solid melting at 165°. A research program was initiated in order to determine which structural features were responsible for the striking differences in the properties of these two all-*cis* diene polymers. The polydimethylenecyclohexane possessed at least four structural features that are not present in natural rubber, increased symmetry, added bulk, presence of a ring and increased hindrance to rotation. In an attempt to determine the effect of steric hindrance on the properties of all-*cis* polymers, 1,2-dimethylenecyclopentane[4] and 3-methyl-1,2-dimethylenecyclohexane[5] were previously prepared. In order to prepare an all-*cis* polymer with a very large amount of steric hindrance, it was of interest to prepare a substituted 1,2-dimethylenecyclohexane with substituents in both the 3- and the 6-positions. Models of the polymer from this substituted diene indicated that rotation would be almost completely restricted.



3,6-Dimethyl-1,2-dimethylenecyclohexane (I) was synthesized in essentially four steps from 2,4-hexadiene in a 30% yield. Thus a mixture of *cis*- and *trans*-2,4-hexadiene, prepared by dehydration

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(1) Previous paper in this series, This Journal, **78**, 2804 (1956).

(2) Office of Naval Research Fellow, 1951–1955.

(3) W. J. Bailey and H. R. Golden, This Journal, **76**, 5418 (1954).

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

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