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.

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(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.

COLLEGE PARK, MARYLAND

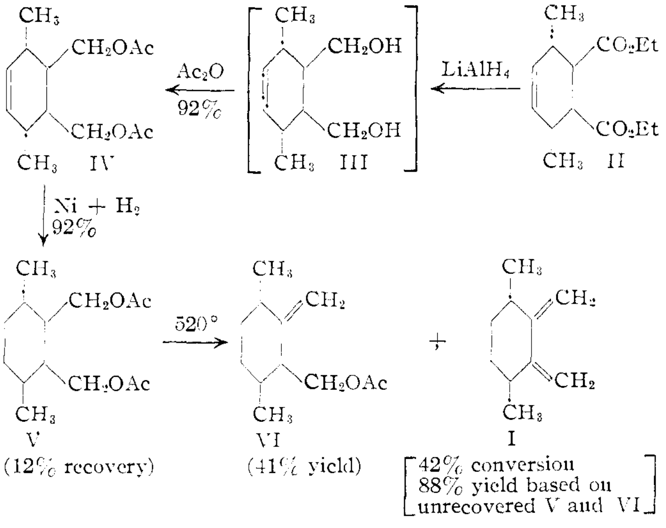
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

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).

of 2-hexen-4-ol over alumina, was treated with maleic anhydride to produce a 44% yield of 3,6-dimethyl-*cis*-Δ^4-tetrahydrophthalic anhydride. However, the small amount of polymer that was invariably formed tended to reduce the yield and made the isolation of the crystalline adduct impractical on a large scale. Therefore, a procedure that avoided the isolation of the solid was employed. When the crude mixture from the reaction of maleic anhydride and 2,4-hexadiene was esterified with ethyl alcohol, diethyl 3,6-dimethyl-*cis*-Δ^4-tetrahydrophthalate (II) could be conveniently isolated by distillation in a 40% yield. Reduction of II with lithium aluminum hydride gave a 75% yield of the 3,6-dimethyl-*cis*-Δ^4-tetrahydrophthalyl alcohol (III). However, if the viscous diol III was not isolated but the crude reduction mixture was acetylated with acetic anhydride, 3,6-dimethyl-*cis*-Δ^4-tetrahydrophthalyl diacetate (IV) was obtained in a 92% over-all yield for the two steps. Catalytic reduction of IV gave a 92% yield of the saturated diacetate V.

The diacetate V was then pyrolyzed under almost the same conditions that were used successfully for the pyrolysis of other strained dienes.[6] Thus a pure diene could be prepared in high yield if carbonization was avoided by the flushing of the pyrolysis tube with oxygen-free nitrogen and by selection of conditions so mild that only about two-thirds of the theoretical amount of acetic acid was liberated. When V was dropped through the Vycor tube packed with glass helices and heated at 520°, 62% of two molar equivalents of acetic acid was liberated. Under these conditions no charring took place, and a 42% conversion to 3,6-dimethyl-1,2-dimethylenecyclohexane (I) was realized. At the same time, 12% of the starting diacetate V was recovered, and a 41% yield of the intermediate 3,6-dimethyl-1-methylene-2-acetoxymethylcyclohexane (VI), which could be recycled to obtain additional diene I, was obtained. The yield of the diene I, based on unrecovered V and VI, was therefore 88%.

The presence of two conjugated exocyclic double bonds in I was indicated by the fact that the ultraviolet absorption spectrum did not possess a maximum or minimum above 220 mμ, but the extinction coefficient increased rapidly as the wave length became shorter and appeared to reach a maximum just below 220 mμ. Conjugated exocyclic double bonds in which the double bonds are not coplanar absorb at wave lengths[6,7] lower than predicted by Woodward's rules.[8] 1,2-Dimethylenecyclohexane possesses an absorption maximum at 220 mμ.[6a] The structure of I also was confirmed by strong absorption bands in the infrared[7] at 864, 895 and 2900 cm.$^{-1}$ and weaker bands at 758, 1375, 1450 and 1535 cm.$^{-1}$. Comparison of the relative intensities of the methyl band (1375 cm.$^{-1}$) and the internal methylene band (1450 cm.$^{-1}$) in the spectrum of I with those in the spectrum of 3-methyl-1,2-dimethylenecyclohexane[5] leads to the conclusion that I possesses more than one methyl group. This would eliminate any possibility that the 2,4-hexadiene had undergone rearrangement either before or during the Diels–Alder reaction. Maleic anhydride reacts with the diene I in a Diels–Alder reaction to produce a 90% yield of 5,8-dimethyl-$\Delta^{9(10)}$-octahydronaphthalene-2,3-dicarboxylic anhydride (VII).

The successful synthesis of this strained diene I, together with the previous reports in this series,[1-6] illustrates that the pyrolysis of esters is a general method of synthesis. The results of polymerization of this diene will be reported separately.

Experimental[9]

Diethyl 3,6-Dimethyl-*cis*-Δ^4-tetrahydrophthalate (II).—A mixture of 87 g. (0.89 mole) of maleic anhydride, 500 ml. of benzene and 1 g. of *p*-*t*-butylcatechol was cooled in an ice-bath. To this solution was added 87 g. (1.06 moles) of a mixture of *cis*- and *trans*-2,4-hexadiene, b.p. 75–83° (reported[10] b.p. 78–82°), and the resulting solution was allowed to stand in an ice-box for 5 days. After the solvent and unreacted diene were removed by distillation under partial vacuum, the residue was dissolved in 550 ml. of benzene and placed in a 2-liter flask equipped with a Dean–Stark distilling receiver. To this solution were added 138 g. (3.0 moles) of absolute ethyl alcohol and 5 g. of concentrated sulfuric acid. This mixture was heated under reflux for 6 days until no more aqueous phase separated in the trap. The cooled reaction mixture was then poured into ice-water and the layers were separated. After the organic layer was dried over anhydrous potassium carbonate, the solvents were removed by evaporation. The residue was distilled through a 6-inch, helix-packed column to yield 107 g. (40% yield based on the hexadiene) of the diethyl 3,6-dimethyl-*cis*-Δ^4-tetrahydrophthalate (II), b.p. 104–105° (0.7 mm.), $n^{25}\text{D}$ 1.4649.

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.11; H, 8.88.

3,6-Dimethyl-*cis*-Δ^4-tetrahydrophthalyl Alcohol (III).—To a mixture of 37 g. of lithium aluminum hydride and 1000 ml. of dry ether was added dropwise with stirring 176 g. (0.695 mole) of diethyl 3,6-dimethyl-*cis*-Δ^4-tetrahydrophthalate (II) dissolved in its own volume of dry ether. At the completion of the addition a heavy precipitate settled out which was broken up only by vigorous stirring. The reaction mixture was then stirred for an additional 6 days at room temperature without any further difficulty. To the reaction mixture, cooled in an ice-bath, was added dropwise 100 ml. of water, followed by the slow addition of 10% hydrochloric acid until nearly all the salts were dissolved. The layers were separated and the aqueous phase was extracted for 48 hr. in an exhaustive ether extractor. The combined ether solutions were dried over anhydrous potassium carbonate, and the ether was evaporated to give the crude viscous glycol. The crude product was distilled through a 6-inch, helix-packed column to yield 88 g. (75%) of 3,6-dimethyl-*cis*-Δ^4-tetrahydrophthalyl alcohol (III), b.p. 130° (0.7 mm.), $n^{25}\text{D}$ 1.5055.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.85; H, 10.45.

3,6-Dimethyl-*cis*-Δ^4-tetrahydrophthalyl Diacetate (IV). A. From 3,6-Dimethyl-*cis*-Δ^4-tetrahydrophthalyl Alcohol (III).—A mixture of 204 g. (1.2 moles) of 3,6-dimethyl-Δ^4-tetrahydrophthalyl alcohol (III), 860 g. of acetic anhydride and 60 g. of acetic acid was heated under reflux for 96 hr. The excess acetic anhydride and acetic acid were removed by distillation through a 6-inch, helix-packed column under a partial vacuum, and the residue was fractionated through the same column to yield 229 g. (75%) of 3,6-dimethyl-*cis*-Δ^4-tetrahydrophthalyl diacetate (IV), b.p. 120° (1.0 mm.), $n^{25}\text{D}$ 1.4702.

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(6) (a) W. J. Bailey and H. R. Golden, THIS JOURNAL, **75**, 4780 (1953); (b) W. J. Bailey and J. Rosenberg, *ibid.*, **77**, 73 (1955).

(7) W. J. Bailey and W. B. Lawson, *ibid.*, **77**, 1606 (1955).

(8) R. B. Woodward, *ibid.*, **63**, 1123 (1941); **64**, 76 (1942).

(9) The authors are grateful to Dr. Mary Aldridge and Kathryn Gerdeman for the analyses and to Joseph Wenograd for the infrared absorption spectrum. The infrared spectrum was obtained with a Perkin–Elmer model 12-C spectrophotometer modified for double-pass operation. The ultraviolet absorption spectrum was obtained with cyclohexane as the solvent in a Beckman DU spectrophotometer. All melting points are corrected.

(10) L. P. Kyriakides, THIS JOURNAL, **36**, 980 (1914).

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.10; H, 8.64.

B. **From Diethyl 3,6-Dimethyl-*cis*-Δ^4-tetrahydrophthalate** (II).—The crude diol III, prepared from 176 g. (0.659 mole) of II as described above but without the distillation, was acetylated in the same manner as the pure diol III to give 162 g. (92% over-all yield from II) of 3,6-dimethyl-*cis*-Δ^4-tetrahydrophthalyl diacetate (IV), b.p. 120° (1.0 mm.), $n^{25}D$ 1.4702.

3,6-Dimethylhexahydrophthalyl Diacetate (V).—In a high pressure hydrogenation bomb were placed 496 g. (1.96 moles) of 3,6-dimethyl-*cis*-Δ^4-tetrahydrophthalyl diacetate (IV) and 50 g. of W-5 Raney nickel catalyst. The hydrogenation was complete in an hour at 75° and 2600 pounds per square inch of hydrogen. The catalyst was removed by filtration, and the filtrate was distilled through a 6-inch, helix-packed column to yield 460 g. (92%) of 3,6-dimethylhexahydrophthalyl diacetate (V), b.p. 133–134° (2.1 mm.), $n^{25}D$ 1.4621.

Anal. Calcd. for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.82; H, 9.53.

3,6-Dimethyl-1,2-dimethylenecyclohexane (I) **and 3,6-Dimethyl-1-methylene-2-acetoxymethylcyclohexane** (VI).—By the use of the pyrolysis apparatus described previously,[6] 91.5 g. (0.38 mole) of 3,6-dimethylhexahydrophthalyl diacetate (V) was dropped through a helix-packed vertical Vycor tube at a temperature of 515–520° at the rate of 1.5 g. per minute. The addition was conducted in an inert atmosphere by introduction of a slow stream of oxygen-free nitrogen at the top of the column. The pyrolysate was collected in a receiver cooled in a Dry Ice–acetone-bath. The pyrolysis products were dissolved in ether and washed free from acetic acid with distilled water. (Titration of the aqueous washings indicated that 62% of two molar equivalents of acetic acid had been liberated.) The ether solutions were dried over anhydrous magnesium sulfate, and the ether was removed by distillation through a 6-inch, helix-packed column. The residue was fractionated through the same column under reduced pressure to yield 20 g. (42%) of 3,6-dimethyl-1,2-dimethylenecyclohexane (I), b.p. 50° (15 mm.) $n^{25}D$ 1.4682; 28.5 g. (41%) of 3,6-dimethyl-1-methylene-2-acetoxymethylcyclohexane (VI), b.p. 86° (2.0 mm.), $n^{25}D$ 1.4665; and 11.5 g. (12% recovery) of the starting diacetate V. The yield of diene I, based on unrecovered V and VI, was 88%.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.38; H, 11.90. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.62; H, 10.25.

5,8-Dimethyl-$\Delta^{9(10)}$-octahydronaphthalene-2,3-dicarboxylic Acid (VII).—To a solution of 2.45 g. (0.025 mole) of maleic anhydride in 75 ml. of ether was added 3.40 g. (0.025 mole) of 3,6-dimethyl-1,2-dimethylenecyclohexane (I). After the solution was heated under reflux for 12 hr., the solvent was removed by evaporation to yield 5.3 g. (90%) of the crude white crystalline 5,8-dimethyl-$\Delta^{9(10)}$-octahydronaphthalene-2,3-dicarboxylic acid (VII), m.p. 136–138°. Three recrystallizations from ether produced an analytically pure sample, m.p. 150.5–151°.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 72.02; H, 7.84.

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[CONTRIBUTION NO. 1341 FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

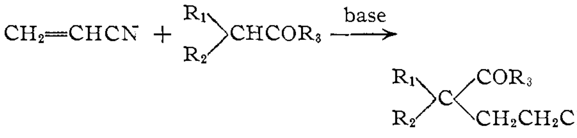
The Reaction of Acrylonitrile with Benzaldehyde under Cyanoethylation Conditions

BY HARRY H. WASSERMAN, B. SURYANARAYANA AND DAVID D. GRASSETTI

RECEIVED DECEMBER 21, 1955

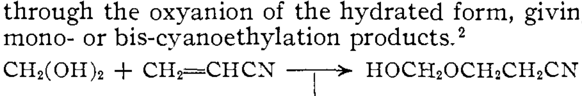
In the presence of Triton B or potassium hydroxide, benzaldehyde reacts with acrylonitrile to form mono- and bis-benzylidene derivatives of β,β'-dicyanodiethyl ether. Other products formed in the presence of potassium hydroxide are α-benzylidene-β-hydroxypropionitrile and β-phenyl-α-formylacrylonitrile. The latter aldehyde is, very probably, formed through an Oppenauer type oxidation of the intermediate unsaturated alcohol. Infrared evidence is presented in support of the assigned structures, and pertinent degradative and synthetic work is described. The stereochemical assignments are based on ultraviolet absorption spectral data.

The reactions of acrylonitrile with aldehydes and ketones containing α-hydrogen atoms have been extensively studied by Bruson and co-workers.[1] These reactions, which take place in the presence of alkaline catalysts, involve a Michael type addition of the carbanion to the activated double bond, and result in the attachment of one or more cyanoethyl residues α to the carbonyl group, as shown



$$CH_2{=}CHCN + (R_1)(R_2)CHCOR_3 \xrightarrow{\text{base}} (R_1)(R_2)C(COR_3)(CH_2CH_2CN)$$

Formaldehyde, having no active hydrogen atoms shows exceptional behavior and appears to react through the oxyanion of the hydrated form, giving mono- or bis-cyanoethylation products.[2]



$$CH_2(OH)_2 + CH_2{=}CHCN \longrightarrow HOCH_2OCH_2CH_2CN;\quad \downarrow\ CH_2(OCH_2CH_2CN)_2$$

In the case of aromatic aldehydes such as benzaldehyde, where there is no active hydrogen, reaction with acrylonitrile takes place under the usual cyanoethylation conditions[1] but the nature of the products formed from these reactions has not previously been established. In connection with other studies, we have reinvestigated this reaction, and are now presenting evidence for the structures of the various products formed.

When acrylonitrile is treated in the cold with benzaldehyde (2:1 molar ratio) using *t*-butyl alcohol as solvent,[3] and in the presence of either Triton B (benzyltrimethylammonium hydroxide) or potassium hydroxide, two main products are formed: A, $C_{13}H_{12}N_2O$, and B, $C_{20}H_{16}N_2O$. Other products formed in smaller yields (in the potassium hydroxide catalyzed reaction) are the alcohol C, $C_{10}H_9ON$, and an aldehyde D, $C_{10}H_7ON$.

Products A and B are neutral, show no carbonyl or hydroxyl absorption in the infrared, but do exhibit strong bands in the nitrile region. A has bands at both 2265 and 2224 cm.$^{-1}$, while B shows only 2229 cm.$^{-1}$ absorption. The ultraviolet ab-

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(1) H. A. Bruson and T. W Riener, THIS JOURNAL, **64**, 2850 (1942); U. S. Patent 2,353,687 (July 18, 1944); *C. A.*, **38**, 6432 (1944).

(2) J. F. Walker, U. S. Patent 2,352,671 (July 4, 1944), *C. A.*, **39**, 223 (1945).

(3) The reaction is carefully maintained at a temperature below 30° to minimize the reaction with solvent.