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

Cyclic Dienes. XV. 3-Methyl-1,2-dimethylenecyclohexane[1]

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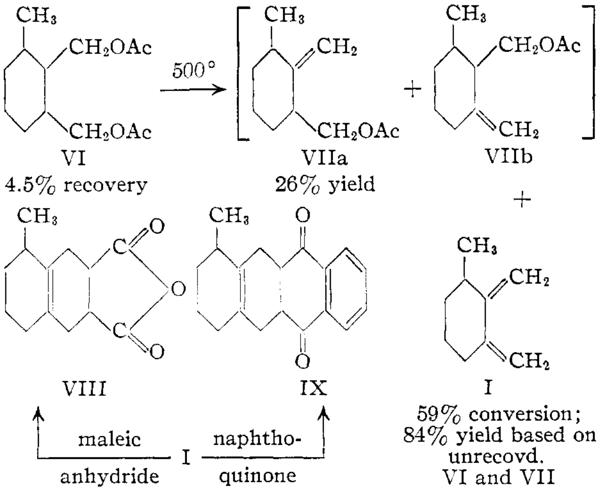
3-Methyl-1,2-dimethylenecyclohexane was synthesized by essentially a four-step procedure from a commercial mixture of *cis*- and *trans*-1,3-pentadiene in a 15% yield. In the crucial step a diacetate was pyrolyzed to the strained diene in an 84% yield, based on unrecovered material. The structure of the diene was proved by analysis, ultraviolet and infrared absorption spectra and conversion through Diels–Alder reactions to two solid derivatives.

Although it is an all-*cis* diene polymer related in structure to natural rubber, poly-1,2-dimethylenecyclohexane[3] possesses no rubbery properties at room temperature but is a white crystalline solid melting at 165°. A research program, therefore, was designed to determine the reason for the striking difference in the properties of these two all-*cis* polymers. It was possible that the greater steric hindrance to rotation in the polydimethylenecyclohexane compared to that in natural rubber was responsible for the high softening point of the synthetic polymer. For this reason, 1,2-dimethylenecyclopentane[4] was previously prepared. The five-membered rings in poly-1,2-dimethylenecyclopentane would obviously allow less steric hindrance than the six-membered rings in poly-1,2-dimethylenecyclohexane. In order to prepare an all-*cis* polymer with a large amount of steric hindrance to rotation, it was of interest to prepare a substituted 1,2-dimethylenecyclohexane with a substituent in the 3-position.

3-Methyl-1,2-dimethylenecyclohexane (I) was prepared in a four-step synthesis from 1,3-pentadiene in an over-all yield of 15%. A commercial mixture of *cis*- and *trans*-1,3-pentadiene was treated with an excess of maleic anhydride at 0° and, without isolation of the adduct, the crude mixture was esterified with ethyl alcohol to produce diethyl 3-methyl-*cis*-Δ^4-tetrahydrophthalate (II) in a 24% yield. Reduction of the ester II with lithium aluminum hydride, followed by acetylation of the product with acetic anhydride without isolation of the intermediate diol, produced an 81% yield of 3-methyl-Δ^4-tetrahydrophthalyl diacetate (III).

An alternative method for the preparation of the unsaturated diacetate III was investigated but was found to be less convenient for the preparation of large amounts, even though it gave a slightly higher over-all yield than the above procedure. By a modification of the method of Farmer and Warren,[5] the mixture of *cis*- and *trans*-1,3-pentadiene was treated with maleic anhydride to produce a 30% yield of 3-methyl-Δ^4-tetrahydrophthalic anhydride (IV). However, this procedure was not adaptable for large-scale preparations since the solid IV was difficult to separate from the polymer which was invariably formed in a side reaction. Experiments with larger quantities of reactants also consistently gave lower yields. Reduction of IV with lithium aluminum hydride produced 3-methyl-*cis*-Δ^4-tetrahydrophthalyl alcohol (V) in a 77% yield. The low solubility of IV in ether complicated the reduction and limited the amount that could be reduced conveniently at one time. Acetylation of V with acetic anhydride produced the diacetate III in a 94% yield.



The unsaturated diacetate III was readily reduced with Raney nickel to give 3-methylhexahydrophthalyl diacetate (VI) in a 93% yield. VI was pyrolyzed under conditions that proved so successful for the synthesis of other cyclic dienes.[6] Thus the diacetate VI was pyrolyzed under such conditions that 78% of two molar equivalents of acetic acid was liberated. Under these conditions no carbonization occurred and a 59% conversion to 3-methyl-1,2-dimethylenecyclohexane (I) was realized. At the same time there was obtained a 26% yield of an olefin acetate VII [presumably a mixture of 3-methyl-2-methylene-1-acetoxymethylcyclohexane (VIIa) and 3-methyl-1-methylene-2-acetoxymethylcyclohexane (VIIb)] and a 4.5% recovery of the starting diacetate VI. The yield of the diene I, based on unrecovered VI and VII, was 84%. As was found previously,[6] if a higher temperature or other more vigorous conditions were employed so that more acetic acid was liberated, charring, which reduced both the yield and the purity of the cyclic diene, took place.

The structure of the 3-methyl-1,2-dimethylenecyclohexane (I) was proved by analysis, ultraviolet and infrared absorption spectra and conversion to two solid derivatives. The ultraviolet absorption spectrum, which shows no maximum above 220 $m\mu$ but increases sharply and appears to reach a maximum just below 220 $m\mu$, indicates the presence of

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[1] Previous paper in this series, THIS JOURNAL, **77**, 1606 (1955).

[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] E. H. Farmer and F. L. Warren, *J. Chem. Soc.*, 3221 (1931).

[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).

two exocyclic conjugated double bonds. Conjugated exocyclic double bonds that are not coplanar absorb at lower wave lengths[1] than predicted by Woodward's rules.[7] 1,2-Dimethylenecyclohexane possesses an absorption maximum at 220 mμ.[6a] On the other hand, 3-methylenecyclohexene[8] has one exocyclic and one endocyclic double bond, has an absorption maximum at 227 mμ as predicted by Woodward's rules.[7] The infrared absorption spectrum of I was very similar to those of other substituted 1,2-dimethylenecyclohexanes reported in this series.[9]

In Diels–Alder reactions the cyclic diene I reacted with maleic anhydride to form 8-methyl-$\Delta^{9(10)}$-octahydronaphthalene-2,3-dicarboxylic anhydride (VIII) and with 1,4-naphthoquinone to form 1-methyl-1,2,3,4,5,5a,6,11,11a,12-decahydronaphthacene-6,11-dione (IX). 3-Methylenecyclohexene does not form an adduct under the conditions used for these reactions.

Copolymerization of I and 1,2-dimethylenecyclohexane to form high molecular weight products will be reported separately.

Experimental[10]

Diethyl 3-Methyl-*cis*-Δ^4-tetrahydrophthalate (II).—To a solution of 763 g. (7.76 moles) of maleic anhydride in 2 liters of dry benzene containing 2 g. of *p*-*t*-butylcatechol cooled to 0° was added dropwise a solution of 544 g. (8.0 moles) of 1,3-pentadiene (Eastman Kodak Co.) in 1 liter of benzene. After the addition was complete, the reaction mixture was allowed to stand at 0° for 5 days. The solvent and unreacted 1,3-pentadiene were removed by distillation under reduced pressure, and the viscous residue treated with 2200 ml. of benzene, 644 g. of absolute ethanol and 5 g. of concentrated sulfuric acid. The mixture was then heated under reflux for 48 hours until no more aqueous phase separated in a Dean-Stark trap. The cooled mixture was poured into 1 l. of ice-water and the organic layer was washed with a sodium carbonate solution and dried over anhydrous potassium carbonate. The solvent was removed from the dry solution by distillation under reduced pressure, and the residue was distilled through a 6-inch, helix-packed column to yield 458 g. (24%) of diethyl 3-methyl-*cis*-Δ^4-tetrahydrophthalate (II), b.p. 115–120° (2.7 mm.), n^{25}D 1.4604.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.95; H, 8.38. Found: C, 65.23; H, 8.44.

3-Methyl-*cis*-Δ^4-tetrahydrophthalyl Diacetate (III). A. From Diethyl 3-Methyl-*cis*-Δ^4-tetrahydrophthalate (II).—To a solution of 42 g. of lithium aluminum hydride and 1200 ml. of dry ether was added dropwise 190 g. (0.79 mole) of diethyl 3-methyl-*cis*-Δ^4-tetrahydrophthalate (II) dissolved in twice its own volume of anhydrous ether. When the addition was complete, a heavy precipitate separated and prevented further stirring of the mixture. The reaction mixture was allowed to stand for 3 days and then 1350 ml. of 10% hydrochloric acid was added dropwise. The layers were separated and the aqueous layer was extracted for 48 hours in an exhaustive ether-extraction apparatus. The combined ether solutions were dried over anhydrous potassium carbonate and the ether was evaporated to give the crude diol. The crude diol V was then heated under reflux for 6 days with 550 g. of acetic anhydride and 60 g. of acetic acid. The excess acetic anhydride and acetic acid were removed by distillation under partial vacuum, and the residue was fractionated through a 6-inch, helix-packed column to yield 153 g. (81%) of 3-methyl-*cis*-Δ^4-tetrahydrophthalyl diacetate (III), b.p. 129–130° (2.5 mm.), n^{25}D 1.4672.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.95; H, 8.38. Found: C, 65.09; H, 8.20.

B. From 3-Methyl-*cis*-Δ^4-tetrahydrophthalyl Alcohol (V).—After a solution of 92 g. (0.59 mole) of 3-methyl-*cis*-Δ^4-tetrahydrophthalyl alcohol (V), 500 g. of acetic anhydride and 60 g. of acetic acid was heated under reflux for 48 hours, the acetic anhydride and acetic acid were removed by distillation through a 6-inch, helix-packed column under partial vacuum and the residue was fractionated through the same column to yield 132.5 g. (94%) of 3-methyl-*cis*-Δ^4-tetrahydrophthalyl diacetate (III), b.p. 129–130° (2.5 mm.), n^{25}D 1.4672.

3-Methyl-*cis*-Δ^4-tetrahydrophthalic Anhydride (IV).—The procedure of Farmer and Warren[5,11] was modified by the use of a commercial mixture of *cis*- and *trans*-1,3-pentadiene instead of the essentially pure *trans* isomer. A solution of 9.8 g. (0.10 mole) of maleic anhydride, 13.6 g. (0.20 mole) of 1,3-pentadiene (Eastman Kodak Co.) and 1 g. of *p*-*t*-butylcatechol in 300 ml. of benzene was allowed to stand at 0° for 5 days. After the solvent was removed under reduced pressure, the residue was recrystallized from ligroin (60–80°) to yield 5.0 g. (30%) of 3-methyl-*cis*-Δ^4-tetrahydrophthalic anhydride (IV), m.p. 61–62° (reported[5] m.p. 61°). The polymer which was invariably formed made the isolation of IV very difficult and sharply reduced the yield in runs with larger quantities of materials.

3-Methyl-*cis*-Δ^4-tetrahydrophthalyl Alcohol (V).—To a solution of 26 g. of lithium aluminum hydride and 1500 ml. of dry ether was added dropwise 66 g. (0.40 mole) of 3-methyl-*cis*-Δ^4-tetrahydrophthalic anhydride (IV) dissolved in 1000 ml. of dry ether, and the reaction mixture was stirred under reflux for 48 hours. To the reaction mixture, cooled in an ice-bath and vigorously stirred, was added dropwise 100 ml. of water followed by 2 liters of 10% hydrochloric acid. The aqueous layer was extracted for 48 hours in an exhaustive ether extractor and the combined ether solutions were dried over anhydrous potassium carbonate. After the ether was removed by evaporation, the residue was distilled through a 6-inch, helix-packed column to yield 48 g. (77%) of 3-methyl-*cis*-Δ^4-tetrahydrophthalyl alcohol (V), b.p. 129–130° (2.5 mm.), n^{25}D 1.5005.

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.33. Found: C, 68.95; H, 10.07.

3-Methylhexahydrophthalyl Diacetate (VI).—A mixture of 269.5 g. (1.12 moles) of 3-methyl-*cis*-Δ^4-tetrahydrophthalyl diacetate (III) with 25 g. of W-5 Raney nickel catalyst[12] was placed in a high pressure hydrogenation bomb and hydrogenated at 150° and 1400 pounds per square inch of hydrogen. The cooled reaction mixture was filtered to remove the catalyst, and the filtrate was distilled through a 6-inch, helix-packed column to yield 254 g. (93%) of 3-methylhexahydrophthalyl diacetate (VI), b.p. 107° (0.7 mm.), n^{25}D 1.4589.

Anal. Calcd. for $C_{13}H_{22}O_4$: C, 64.43; H, 9.15. Found: C, 64.20; H, 8.97.

3-Methyl-1,2-dimethylenecyclohexane (I).—At the rate of 1.5 g. per minute, 133.5 g. (0.55 mole) of 3-methylhexahydrophthalyl diacetate (VI) was added dropwise to a vertical Vycor combustion tube, packed to a depth of 12 inches with $^1/_8$-inch glass helices and heated externally at 520° by a FD 303A Hoskins furnace. The addition was conducted in an inert atmosphere by the introduction of a slow stream of nitrogen at the top of the column. The pyrolysate was collected in a receiver cooled in a Dry Ice–acetone bath. The pyrolysate was dissolved in ether and washed free of acetic acid with distilled water. The aqueous washings were combined and an aliquot was titrated with standard sodium hydroxide solution. The titration indicated that 78% of two molar equivalents of acetic acid had been liberated. The ether solution was dried over anhydrous magnesium sulfate and the ether was removed by distillation. The residue was fractionated through a 6-inch, helix-packed column under reduced pressure to yield 39.5 g. (59%) of 3-methyl-1,2-dimethylenecyclohexane (I), b.p. 47° (25 mm.),

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

(8) W. J. Bailey and J. C. Goossens, *ibid.*, **78**, in press (1956).

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

(10) 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.

(11) D. Craig, THIS JOURNAL, **65**, 1006 (1943).

(12) H. Adkins and H. R. Billica, *ibid.*, **70**, 695 (1948).

n^{25}_{D} 1.4704; 25.6 g. (26%) of a mixture of 3-methyl-2-methylene-1-acetoxymethylcyclohexane (VIIa) and 3-methyl-1-methylene-2-acetoxymethylcyclohexane (VIIb), b.p. 72° (2.2 mm.), n^{25}_{D} 1.4641; and 6.0 g. (4.5% recovery) of unchanged diacetate VI. The yield of the diene I, based on unrecovered VI and VII, was 84%. Strong absorption bands in the infrared at 895 and 2900 cm.$^{-1}$ and medium strong bands at 839, 860, 1450 and 1555 cm.$^{-1}$ confirm the structure of I.[9]

Anal. Calcd. for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.73; H, 11.50. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.79; H, 9.74.

8-Methyl-$\Delta^{9(10)}$-octahydronaphthalene-2,3-dicarboxylic Anhydride (VIII).—A mixture of 3.0 g. (0.025 mole) of 3-methyl-1,2-dimethylenecyclohexane (I), 2.0 g. (0.020 mole) of maleic anhydride and 50 ml. of ether was heated under reflux for 1 hour. The reaction mixture was cooled and the resulting precipitate was recrystallized from ether to yield 2.25 g. (41%) of 8-methyl-$\Delta^{9(10)}$-octahydronaphthalene-2,3-dicarboxylic anhydride (VIII), m.p. 124.5–125°.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 71.07; H, 7.27.

1-Methyl-1,2,3,4,5,5a,6,11,11a,12-decahydronaphthacene-6,11-dione (IX).—A mixture of 2.0 g. (0.0125 mole) of 1,4-naphthoquinone, 4.0 g. (0.0328 mole) of 3-methyl-1,2-dimethylenecyclohexane (I), and 100 ml. of ether was heated under reflux for 12 hours. The warm solution was filtered and the filtrate was cooled to precipitate white crystals. Recrystallization from petroleum ether (30–60°) yielded 1.0 g. (29%) of 1-methyl-1,2,3,4,5,5a,6,11,11a,12-decahydronaphthacene-6,11-dione (IX), m.p. 138–139°. Two additional recrystallizations from the same solvent produced an analytical sample, m.p. 141.5–142°.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.17; H, 6.97.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BUCKNELL UNIVERSITY]

Identification of Amines. II. Phthalimidomethyl Derivatives of Primary and Secondary Amines[1]

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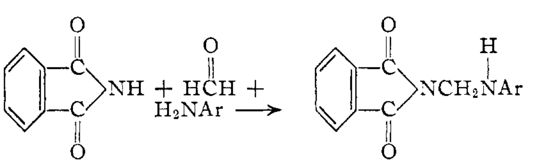
The condensation of phthalimide and formaldehyde with primary aliphatic amines has been shown to yield bis-(phthalimidomethyl)-alkylamines. In addition the syntheses of some N-(arylaminomethyl)-, N-(alkylarylaminomethyl)- and N-(dialkylaminomethyl)-phthalimides are reported.

Recently it has been shown that the condensation of primary aromatic amines with formaldehyde and phthalimide can be used successfully for the syntheses of N-(arylaminomethyl)-phthalimides,[2] *i.e.*


(1)

These compounds are useful for the characterization of amines since they are easily prepared and purified and have sharp melting points. The scope of the reaction which in some aspects is similar to the Mannich condensation has now been extended to aliphatic primary and secondary amines as well as aromatic secondary amines. No difficulty was encountered with the formation of the phthalimidomethyl derivatives of the aliphatic and aromatic secondary amines listed in Table I except that the yields were lower than were observed for the primary aromatic amines.[2] The primary aliphatic amines differed markedly, however, from the primary aromatic amines in that they readily formed the bis-(phthalimidomethyl)-alkylamines, (II). The results are in harmony with the recent observations of Haworth and co-workers[3] who reported that the condensation of the N-hydroxymethyl derivatives of benzamide, phenylacetamide and β-phenylpropionamide (formed by reaction of formaldehyde and the amides under alkaline conditions) with methylamine formed tertiary amino derivatives of the type shown in equation II. A similar product was reported for the reaction of N-hydroxymethylbenzamide with *n*-butylamine.[3]

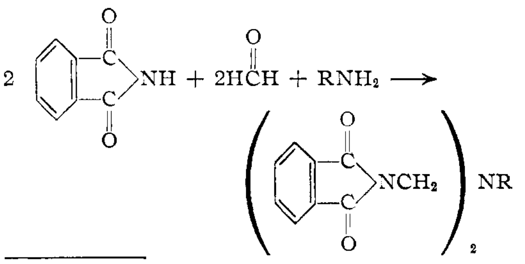

(II)

Table I lists twenty-four additional N-(arylaminomethyl)-phthalimides of primary aromatic amines as well as seven N-(alkylarylaminomethyl)-phthalimido derivatives of secondary aromatic amines. Also included in Table I are six N-(dialkylaminomethyl)-phthalimide derivatives of secondary aliphatic amines. The bis-(phthalimidomethyl)alkylamines are presented in Table II.

Experimental

N-(Arylaminomethyl)-phthalimide and N-(Alkylarylaminomethyl)-phthalimide Derivatives.—It was found convenient to modify the original procedure for the preparation of these compounds as follows.[2] Three grams (0.0204 mole) of phthalimide was suspended in 35 ml. of 95% ethanol. Two milliliters of 37% formaldehyde was added and reflux was begun. Next 0.023 mole of the primary or secondary aromatic amine was added to the hot alcoholic solution. The solution turned yellow immediately. At this point the alcoholic solution was usually homogeneous and was refluxed for one-half hour. In a few cases the derivative began to separate from the boiling solution shortly after reflux was begun. Whenever this occurred reflux was discontinued

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(1) This paper represents a portion of a thesis submitted by Robert P. Blair, in partial fulfillment of the requirements for the degree of Master of Science, Bucknell University, July, 1955.

(2) M. B. Winstead and H. W. Heine, THIS JOURNAL, **77**, 1913 (1955).

(3) R. D. Haworth, D. H. Peacock, W. R. Smith and R. MacGillivray, *J. Chem. Soc.*, 2972 (1952).