Cyclic Dienes. XXVI. 5-Methylene-1,3-cyclohexadiene, an Alicyclic Isomer of Toluene[1-3]

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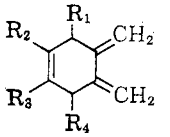
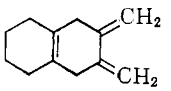
5-Methylene-1,3-cyclohexadiene, isomeric with toluene, was prepared by the pyrolysis of 1,4-cyclohexadiene-1-methanol methyl carbonate, followed by isolation with a gas chromatographic column. The structure of the triene was proved by its infrared and ultraviolet spectra, conversion to a solid Diels-Alder adduct, and isomerization to toluene.

Since the syntheses of 4,5-dimethylenecyclohexene[5] (I) and 3,6-dimethylenecyclohexene[6] (II) together with their homologs[7,8] were accomplished in high yields from their corresponding acetates, without the formation of any of the corresponding isomeric aromatic compounds,





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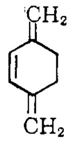
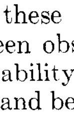


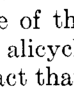
II

I. $R_1 = R_2 = R_3 = R_4 = H$
Ia. $R_1 = R_3 = R_4 = H, R_2 = CH_3$
Ib. $R_1 = R_4 = H, R_2 = R_3 = CH_3$
Ic. $R_1 = R_4 = CH_3, R_2 = R_3 = H$

an interesting extension of the synthesis of nonaromatic isomers appeared to be the synthesis of the isomers of toluene. Two alicyclic isomers of toluene can be written in which the hydrogen from the methyl group is shifted to the *ortho-* and *para-*carbon atoms, as in III and IV, respectively.



III



IV

Mention of the isomers III and IV was made by Horning,[9] who speculated on the possibility of their existence. In fact, he stated that "the independent existence of these isomers as chemical individuals has never been observed because of the great difference in stability between the alicyclic and aromatic forms and because of the fact that the transition to the aromatic form occurs with such readiness that there is no way of preventing it."

Summing up his observations, Horning stated: "In the event that the aromatization (of compounds such as III and IV) required a rearrangement of hydrogen atoms that can be accomplished by a single tautomeric shift such as that of the keto-enol variety, the alicyclic isomers of benzene and naphthalene series have no existence as chemical individuals, so far as is now known. Any preparative method designed to yield such a compound results in the isomer instead, simply because of the ease with which the tautomeric shift is brought about." The "great difference in stability between the alicyclic and aromatic forms" associated with the tremendous increase in resonance energy accompanying the rearrangement of the alicyclic to the aromatic forms may be estimated to be about 25 to 30 kcal.[10]

An examination of the three cyclohexadienemethanols which are possible precursors of III revealed that 1,4-cyclohexadiene-1-methanol (V) was quite attractive as well as the most convenient to synthesize. Propiolic acid was allowed to react with 1,3-butadiene to give an almost quantitative yield of 1,4-cyclohexadiene-1-carboxylic acid (VI), which was readily reduced with lithium aluminum hydride in an 85% yield to the alcohol V. Esterification of V with methyl chloroformate in the presence of pyridine afforded 1,4-cyclohexadiene-1-methanol methyl carbonate (VII) in a 76% yield. A solution of VII in methanol (1:3 ratio by weight) was pyrolyzed through a Vycor tube packed with new Pyrex helices, and the pyrolysate was collected in a flask immersed in a Dry Ice–Methyl Cellosolve bath. The pyrolysate obtained in this way contained 5-methylene-1,3-cyclohexadiene (III) and toluene in approximately a 1:9 ratio. During pyrolysis the ester group of VII was presumed to undergo an allylic rearrangement prior to the formation of III.[11]

The triene III was concentrated, first by the azeotropic distillation of the pyrolysate followed by

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[1] Previous paper in this series, *J. Org. Chem.*, **25**, 511 (1960).

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[4] Goodyear Tire and Rubber Fellow, 1957–1958.

[5] W. J. Bailey and J. Rosenberg, *J. Am. Chem. Soc.*, **77**, 73 (1955).

[6] W. J. Bailey and R. Barclay, Jr., *ibid.*, **81**, 5393 (1959).

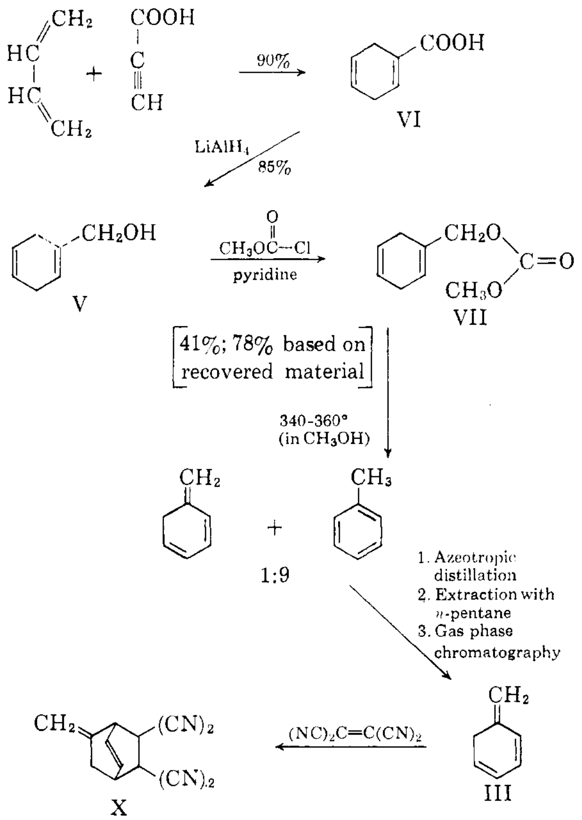
[7] W. J. Bailey, J. Rosenberg, and L. J. Young, *ibid.*, **77**, 1163 (1955).

[8] W. J. Bailey, R. L. Hudson, and C. W. Liao, *ibid.*, **80**, 4358 (1958).

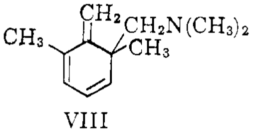
[9] E. C. Horning, *Chem. Rev.*, **33**, 89 (1943).

[10] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaugham, *J. Am. Chem. Soc.*, **58**, 164 (1936); J. B. Conn, G. B. Kistiakowsky, and H. A. Smith, *ibid.*, **61**, 1868 (1939).

[11] W. J. Bailey and R. Barclay, Jr., *J. Org. Chem.*, **21**, 328 (1956); W. J. Bailey and J. C. Goosens, *J. Am. Chem. Soc.*, **78**, 2804 (1956).

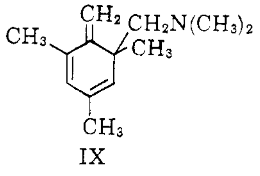


extraction of the distillate with a minimum amount of n-pentane. (The n-pentane extracts could be kept at the Dry Ice temperature indefinitely without any detectable loss of the triene III.) An 87% recovery of the starting ester VII was obtained by distillation of the residue from the azeotropic distillation. The separation of all of the components of the n-pentane extractions and collection of pure III were accomplished by a preparative gas-phase chromatographic column. The triene III was characterized by an ultraviolet absorption, $\lambda_{\max}$ 303 mμ, ϵ 4400. Hauser[12] had synthesized the analogs VIII and IX of 5-methylene-1,3-cyclohexadiene (III) while studying an anomalous Somelet reaction. Since the trienes VIII and IX have ultraviolet absorptions at 308 and 313 mμ, respectively,



VIII

$\lambda_{\max}$ 308 mμ



IX

$\lambda_{\max}$ 313 mμ

from an application of Woodward's rule,[13] one would predict that 5-methylene-1,3-cyclohexadiene (III) would have an absorption at 303 mμ.

The infrared absorption of III showed strong bands at 3020, 2900, 1595, 1400, 864, 692, and 645 cm.$^{-1}$; medium bands at 2850, 1152, and 790 cm.$^{-1}$; and weak bands at 1550, 955, and 910 cm.$^{-1}$.

The structure of III further was proved by its conversion to toluene (1) with platinum in the presence of hydrogen, and (2) at room temperature in an infrared microcell. A portion of the original n-pentane solution was used to give a solid Diels-Alder adduct X with tetracyanoethylene.

5-Methylene-1,3-cyclohexadiene (III) is quite stable at the Dry Ice temperature and in dilute solutions, as shown by its stability at elevated temperatures (110°) in the gas-phase chromatographic column, but in the pure liquid it isomerizes to toluene at a moderately rapid rate at room temperature. These data clearly show the efficacy of the pyrolysis of esters to synthesize highly unstable isomers of aromatic compounds. Although the isomer III was subjected to a temperature of 360° in the pyrolysis tube, the fact that III undergoes isomerization to toluene even at room temperature suggests that the pyrolysis of esters is, indeed, a very mild reaction.

Experimental[14]

1,4-Cyclohexadiene-1-carboxylic Acid (VI).—Propiolic acid, b.p. 77–80° (48 mm.) [reported[15] b.p. 53–54.5° (12 mm.)], was prepared in a 50% yield by the oxidation of propargyl alcohol with chromium trioxide by the procedure of Wolf. Into a Carius tube containing 40 g. (0.57 mole of propiolic acid immersed in a Dry Ice–Methyl Cellosolve mixture was distilled 40 g. (1.2 moles) of butadiene. The sealed tube was placed in a hydrogenation vessel and heated at 80° for 1 hr. A nearly quantitative yield, 68 g. (96%), of 1,4-cyclohexadiene-1-carboxylic acid (VI), m.p. 122–123° (reported[16] m.p. 121–122°), was obtained.

1,4-Cyclohexadiene-1-methanol (V).—To a slurry of 28 g. (0.74 mole) of lithium aluminum hydride in 1 l. of anhydrous ether contained in a 3-l., three-necked flask, equipped with a stirrer, a reflux condenser and a dropping funnel, was added 2 liters of an ether solution containing 90 g. (0.725 mole) of 1,4-cyclohexadiene-1-carboxylic acid (VI) over a period of 1 hr. When the addition was completed, the mixture was heated under reflux for an additional 20 hr. After the mixture had cooled, a saturated aqueous solution of Rochelle salt (*ca.* 50 ml.) was added to the mixture until coagulation of complex aluminum salts took place. The supernatant liquid was decanted, and the solid was washed with several portions of ether. After the combined decanted solution and washings were dried over anhydrous magnesium sulfate, distillation through a 6-in. Vigreux column gave 70 g. (85%) of 1,4-cyclohexadiene-1-methanol (V), b.p. 108–112° (23 mm.), n^{25}D 1.5112.

Anal. Calcd. for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.08; H, 9.28.

1,4-Cyclohexadiene-1-methanol Methyl Carbonate (VII).—To a solution of 80 g. (0.73 mole) of 1,4-cyclohexadiene-1-

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(12) C. R. Hauser, Abstracts of the 15th National Organic Symposium of the American Chemical Society, June, 1957, Rochester, New York, p. 1.

(13) A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," E. Arnold, Ltd., London, 2nd ed., 1957, p. 98.

(14) The authors are grateful to Dr. Franz Kasler, Mrs. Kathryn Baylouny, and Mrs. Jane Ratka for the microanalyses. The authors are also grateful to Dr. E. R. Lippincott and Francis X. Powell for aid in the interpretation of the infrared spectrum. The infrared spectrum was determined on a Beckman IR-5 spectrophotometer with a microcell with a capacity of about 1 ml. The ultraviolet spectra were determined in a Beckman DK-1 spectrophotometer.

(15) V. Wolf, *Ber.*, **86**, 935 (1953).

(16) S. L. Emerman and J. Meinwald, *J. Org. Chem.*, **21**, 375 (1956).

methanol (V) in 180 g. of pyridine was added 90 g. (0.95 mole) of methyl chloroformate while the solution was stirred and cooled with an ice-water bath. Then the mixture was allowed to warm to room temperature and was heated on a steam bath for 2 hr. After the reaction mixture had cooled, 100 ml. of ether was added and again the mixture was heated under reflux for several minutes. The white precipitate was removed by filtration and washed with ether. The combined filtrate and ether washings were washed successively with 5% hydrochloric acid, until the washings were slightly acid toward litmus, with 100 ml. of 5% sodium bicarbonate solution, and finally with 100 ml. of water. After the ethereal solution had been dried over anhydrous magnesium sulfate, the precipitate was removed by filtration and the ether was removed by evaporation. Distillation of the residue yielded 37 g. (46% recovery) of the starting alcohol V and 52 g. (41%) of 1,4-cyclohexadiene-1-methanol methyl carbonate (VII), b.p. 76.5° (3 mm.), $n^{25}\text{D}$ 1.4768. The yield of VII, based on unrecovered V, was 76%.

Anal. Calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.49; H, 7.29.

Pyrolysis of 1,4-Cyclohexadiene-1-methanol Methyl Carbonate (VII).—A solution of 20 g. (0.12 mole) of 1,4-cyclohexadiene-1-methanol methyl carbonate (VII) in 60 g. of anhydrous methanol was dropped through a helix-packed Vycor tube heated at 340–360° by a Hoskins electric furnace, as described previously.[17] In order to prevent the pyrolysate from solidifying, an additional 60 g. of methanol was added through an addition tube to the pyrolysate before it entered the flask immersed in the Dry Ice–Methyl Cellosolve mixture. The pyrolysate was distilled under aspirator pressure (20–40 mm.) at room temperature, and the distillate was condensed in a trap cooled in a Dry Ice–Methyl Cellosolve mixture. After this distillate was mixed with an equal volume of cold (0–5°) distilled water, the resulting aqueous solution was extracted with a minimum amount (15 to 20 1-ml. portions) of *n*-pentane. This extraction was best done in a volumetric flask where the desired organic phase could be easily removed by a pipet at the top. The *n*-pentane extracts may be stored indefinitely in a vial cooled in a Dry Ice–methyl Cellosolve mixture without appreciable loss of the triene III.

5-Methylene-1,3-cyclohexadiene (III).—Isolation of 5-methylene-1,3-cyclohexadiene (III) from the pentane solution described above was accomplished by the use of a gas-phase chromatographic column (11 mm. × 2 m.) packed with 30% polyethylene glycol E1000 on 30–60 mesh Chromosorb. The column temperature was maintained at 70° and the helium flow rate, as determined by a soap film buret flowmeter, was regulated to about 2 ml. per second. Under these conditions, toluene and the triene III had retention times of 15 and 18 min., respectively. From 0.2 to 1.0 ml. of the *n*-pentane solution was introduced into the column without interference of *n*-pentane with the collection of the isomer III. Collection of the compound was made by the condensation of the vapors in a modified U-tube. The vapors were directed *via* a large needle (gage 18) into one end of the tube, while the other end contained a tube of indicating Drierite for protection against moisture.

At the time of collection, the apparatus was connected to the exit tube of the thermistor block and the lower part of the U-tube was immersed in a Dry Ice–Methyl Cellosolve mixture. Generally, the collection was begun about 5 to 10 sec. following the initial response of the recorder pen at the desired peak. By use of the apparatus and procedure described above about 5 to 10 mg. of 5-methylene-1,3-cyclohexadiene (III) was collected at a time and the liquid collected from many runs was used to obtain the data, unless otherwise stated.

Anal. Calcd. for C_7H_8: C, 91.30; H, 8.74. Found: C, 91.07; H, 8.78.

The ultraviolet absorption spectrum of a sample of III (containing no more than 2 to 3% toluene) was determined in isooctane solution (1.25×10^{-4} mole/l.) to be $\epsilon_{\max}$ of 4400 at 303 mμ.

Infrared spectra, determined for the pure liquid III and for its carbon tetrachloride solution, showed strong bands at 3020, 2900, 1595, 1400, 864, 692, and 645 cm.$^{-1}$; medium bands at 2850, 1152, and 790 cm.$^{-1}$; and weak bands at 1550, 955 and 910 cm.$^{-1}$.

2,2,3,3-Tetracyano-7-methylene-5-bicyclo[2.2.2]octene (X).—To 5 ml. of the *n*-pentane extract [from the pyrolysis of 5 g. of 1,4-cyclohexadiene-1-methanol methyl carbonate (VII)] was added a solution of tetracyanoethylene in benzene (0.10 g./10 ml.) until the mixture was faintly yellow (required about 2 ml.). A white solid precipitated and the mixture was filtered to give 34 mg. (95%) of 2,2,3,3-tetracyano-7-methylene-5-bicyclo[2.2.2]-octene (X), m.p. 134–136°.

Anal. Calcd. for $C_{13}H_8N_4$: C, 70.90; H, 3.66. Found: C, 70.60; H, 3.68.

Isomerization of 5-Methylene-1,3-cyclohexadiene (III) to Toluene. A. By Standing at Room Temperature.—About 2 mg. of crude 5-methylene-1,3-cyclohexadiene (III) (some toluene was present in the sample from the start, as shown by this analysis) was placed in an infrared microcell and its spectrum was taken at 45-min. intervals for 3 hr. A marked disappearance of the infrared bands pertaining to III was apparent, concurrent with the appearance of those corresponding to toluene.

B. By Reaction with Platinum in the Presence of Hydrogen.—After a mixture of about 2 mg. of platinum oxide and 2 ml. of absolute ethanol was saturated with hydrogen in a 5-ml. flask, 6.7 mg. of a sample containing 60% of III and 40% of toluene was added to this mixture. The resulting mixture was stirred in an atmosphere of hydrogen for about 2 hr. No hydrogen absorption was observed. The mixture was quantitatively transferred to a small vial (the total volume was 5.3 ml.). After exactly 1 ml. of this solution was dissolved in 2 ml. of absolute ethanol (420 mg./l.), an ultraviolet absorption determination showed that the resulting solution had a maximum optical density of 0.87 at 261 mμ. Since the extinction coefficient at this maximum absorption of toluene is 225[18] at 261 mμ, the concentration of toluene in this solution was calculated to be 360 mg./l. (90%).

To the remainder of the original solution (4.3 ml., containing 5.4 mg. of the sample) was added 26.7 mg. of benzene as an internal standard for gas-phase chromatography. A calculation of the ratio of the areas of benzene and toluene indicated the presence of 4.6 mg. (85%) of toluene in the solution.

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[17] W. J. Bailey and R. A. Baylouny, *J. Am. Chem. Soc.*, **81**, 2126 (1959).

[18] L. Daub and J. M. Vanderbelt, *ibid.*, **69**, 2714 (1947).