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

Pyrolysis of Esters. XIV. Synthesis of 1,3-Dimethylenecyclohexane[1]

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The pyrolysis of hexahydroisophthalyl diacetate at 555° gave a 94% yield of 1,3-dimethylenecyclohexane. This ester was studied since the product possesses the tendency to rearrange to form a conjugated system as well as the driving force of an exocyclic double bond to form an endocyclic double bond. The fact that little or no rearrangement to the conjugated diene occurred indicates that the pyrolysis of esters is a very mild method for the introduction of unsaturation.

The pyrolysis of esters has been shown to be an excellent method for the synthesis of olefins free from isomeric impurities formed by rearrangement.[3,4] This pyrolytic method has been particularly useful for the synthesis of cyclic dienes containing strained double bonds in a series of 1,2-dimethylenecyclohexanes.[5-8]

Even though these exocyclic double bonds are strained, there appears to be little or no tendency for rearrangement under pyrolytic conditions, provided that all carbonization is eliminated.

In order to investigate other highly strained dienes that could be synthesized by pyrolysis, a series[9-11] of isomers of aromatic compounds were prepared. For example, 1,2-dimethylene-4-cyclohexene,[9] isomeric with *o*-xylene, was prepared in a 92% yield by the pyrolysis of a diacetate. It is noteworthy that the Hofmann decomposition of the corresponding bis quaternary ammonium hydroxide gave only *o*-xylene and none of the exocyclic triene.[12] Similarly, the pyrolysis of a diacetate produced an isomer of *p*-xylene, 1,4-dimethylene-2-cyclohexene.[11] Although the driving force for aromatization is strong in each case, rearrangement of both exocyclic double bonds is required. In the former case the aromatization must be initiated by the rearrangement of one of the exocyclic double bonds into conjugation with the internal double bond.

The pyrolysis of esters has been applied to the synthesis of 1,4-dienes with a variety of successes, depending on the conditions. Schniepp and Geller[13] successfully prepared 1,4-pentadiene by the pyrolysis of 1,5-diacetoxypentane. Similarly, Riobé[14] prepared a series of substituted 1,4-pentadienes by pyrolysis of the corresponding unsaturated acetates. Although Paul and Tchelitcheff have used pyrolysis to prepare 1,4-pentadienes,[15] they also have reported several pyrolyses that should have produced only unconjugated dienes but that have given substantial amounts of the conjugated diene.[15,16] In order to evaluate the mildness of this pyrolytic method still further, it seemed of interest to study an ester that combined the driving force for rearrangement of both these systems, that is, to prepare a cyclic diene that would have as the driving force for rearrangement not only the tendency of the unstable double bond exocyclic to a six-membered ring to shift to an internal position but also the tendency of the double bonds to shift into conjugation. Such a diene was 1,3-dimethylenecyclohexane (I). The pyrolysis of the hexahydroisophthalyl diacetate (IV) to produce the diene I was of further interest since it would give a comparison of the ease of pyrolysis of a diacetate to produce an unconjugated diene with that of the previously studied diacetates that produced conjugated dienes.

The preparation of diethyl isophthalate (II) in an over-all yield of 72% was accomplished by the oxidation of *m*-xylene with potassium permanganate to produce isophthalic acid, which was directly esterified with ethanol by the azeotropic method with benzene. The ester II was reduced with Raney nickel under high pressure to produce a mixture of diethyl *cis*- and *trans*-hexahydroisophthalate (III) in a 96% yield. Treatment of III with lithium aluminum hydride, followed by careful acidification of

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(1) Previous paper in this series, *J. Org Chem.*, **23**, 996 (1958).

(2) Office of Naval Research Fellow, 1953–54.

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(8) W. J. Bailey and W. A. Klein, *J. Am. Chem. Soc.*, **79**, 3124 (1957).

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

(10) W. J. Bailey, J. Rosenberg, and L. J. Young, *J. Am. Chem. Soc.*, **77**, 1163 (1955).

(11) W. J. Bailey and R. Barclay, Jr., Abstracts of the 130th National Meeting of the American Chemical Society, Atlantic City, N. J., September 1956.

(12) J. E. Ladbury and E. E. Turner, *J. Chem. Soc.*, 3885 (1954).

(13) L. E. Schniepp and H. H. Geller, *J. Am. Chem. Soc.*, **67**, 54 (1945).

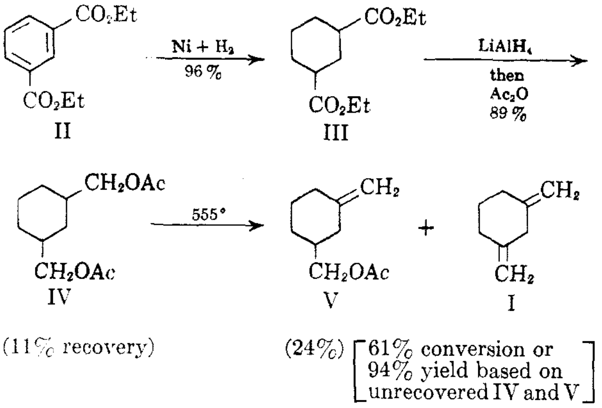
(14) O. Riobé, *Compt. rend.*, **226**, 1625 (1948).

(15) R. Paul and S. Tchelitcheff, *Bull. soc. chim. France*, **15**, 108 (1948).

(16) R. Paul and S. Tchelitcheff, *Compt. rend.*, **223**, 1136 (1946).

the complex, produced a 94% yield of a mixture of *cis*- and *trans*-hexahydroisophthalyl alcohol.

An alternative synthesis of the hexahydroisophthalyl alcohol proceeded in a similar fashion from dimethyl isophthalate. Esterification of this alcohol with acetic anhydride produced a mixture of *cis*- and *trans*-hexahydroisophthalyl diacetate (IV) in a 95% yield.



When the diacetate IV was dropped through a pyrolysis tube packed with glass helices at 555° under such conditions that 75% of two molar equivalents of acetic acid was eliminated, a 61% conversion to 1,3-dimethylenecyclohexane (I) and a 24% yield of 3-methylenehexahydrobenzyl acetate were realized. Since 11% of the starting material IV was recovered unchanged, the yield of the diene I, based on unrecovered IV and V, was 94%. At 515° only 30% of two molar equivalents of acetic acid was eliminated. Under comparable conditions (520°), hexahydrophthalyl diacetate liberated 65% of two molar equivalents of acetic acid.[5] Thus it appears that the production of a conjugated diene appreciably aids the elimination of acetic acid.

The structure of the 1,3-dimethylenecyclohexane (I) was indicated by analysis and ultraviolet and infrared absorption spectra. The absence of conjugated double bonds was indicated by the fact that the ultraviolet absorption spectrum showed no maximum or minimum above 220 mμ and the ϵ was only 25 at 220 mμ. (1,2-Dimethylenecyclohexane[5] has an ϵ maximum of 10,050 at 220 mμ). Similarly, the most likely rearranged product with one double bond exocyclic and the other endocyclic would be expected to have a maximum absorption above 235 mμ.[17]

The infrared absorption spectrum with strong bands at 3065, 2970, 1770, 1642, 1428–1443, 1350, 1250, 1172, 1070, 1042, 998, 970, 900, 940–960, 770, 732, and 676 cm.$^{-1}$ and weaker bands at 1551, 1395, 1335, 1310, 1272, 1178, 1162, 1102, 988, and and 980 cm.$^{-1}$ is consistent with the presence of two unconjugated methylene groups.

It must be concluded that the tendency for rearrangement during the pyrolysis of esters is indeed quite small. This information should make possible the syntheses of other interesting dienes and the preparation of a new series of isomers of aromatic compounds.

EXPERIMENTAL[18]

Diethyl isophthalate (II). A mixture of 106 g. (1.0 mole) of *m*-xylene, 26 g. of sodium hydroxide, 200 g. of potassium permanganate, and 5 l. of water was heated under reflux for 24 hr. until all of the permanganate color had been discharged. At that time an additional 200 g. of potassium permanganate and 26 g. of sodium hydroxide were added and the heating of the mixture was continued. This process was repeated until a total of 1200 g. of permanganate had been added. The excess potassium permanganate was decomposed with ethanol and the manganese dioxide was removed by filtration. The filtrate was acidified with concentrated hydrochloric acid and the precipitate was removed by filtration. This crude isophthalic acid was not purified but was placed in a 5-l., three-necked flask, equipped with two Dean-Stark traps, together with 1 l. of absolute alcohol, 5 l. of benzene, and 5 ml. of concentrated sulfuric acid. After the mixture had been heated under reflux for 8 days and no additional aqueous phase was formed, the solution was concentrated to about 800 ml. by distillation. The concentrate was extracted with water and then with a saturated sodium bicarbonate solution and dried over magnesium sulfate. After the solvents had been removed by distillation under reduced pressure, the residue was fractionated through a 12-inch, helix-packed column to yield 158 g. (72%) of diethyl isophthalate (II), b.p. 150° (0.7 mm.), n_D^{25} 1.5053 [reported[19] b.p. 170–170.5° (24 mm.), $n_D^{17.5}$ 1.50815].

Diethyl hexahydroisophthalate (III). In a 300-ml. hydrogenation vessel, 111 g. (0.50 mole) of diethyl isophthalate (II) was hydrogenated at 80° and 250 atmospheres pressure in the presence of 8 g. of W-2 Raney nickel catalyst.[20] The amount of hydrogen consumed was 103% of the theoretical amount. After the catalyst had been removed by filtration, the filtrate was fractionated through a 10-inch, Vigreux column to yield 108 g. (96%) of a mixture of diethyl *cis*- and *trans*-hexahydroisophthalate (III), b.p. 127–131° (3.5 mm.), n_D^{25} 1.4494 [reported[21] b.p. 141–151° (15 mm.), n_D^{20} 1.4511].

Dimethyl hexahydroisophthalate. In a high pressure hydrogenation vessel, 487 g. (2.51 moles) of dimethyl isophthalate was hydrogenated at 150° and 307 atmospheres pressure in the presence of 50 g. of W-2 Raney nickel catalyst. After the catalyst had been removed by filtration, the filtrate was distilled through a modified Claisen head to yield 494 g. (98%) of a mixture of dimethyl *cis*- and *trans*-hexahydroisophthalate, b.p. 120° (1.5 mm.), n_D^{25} 1.4545 [reported[21] b.p. 139–148° (20 mm.), n_D^{20} 1.4570].

Hexahydroisophthalyl alcohol. A. From diethyl hexahydroisophthalate (II). To a slurry of 27 g. (0.71 mole) of lithium aluminum hydride in 1000 ml. of ether contained in a 3-l., three-necked flask, equipped with a stirrer, a condenser, and a dropping funnel, was added dropwise 99 g. (0.435 mole) of

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[17] W. J. Bailey and J. C. Goossens, *J. Am. Chem. Soc.*, **78**, 2804 (1956).

[18] The authors are indebted to Dr. Mary Aldrich and Kathryn Gerdeman for the microanalyses and to Kathryn Gerdeman and Dr. Robert A. Spurr for the infrared spectrum. The infrared absorption spectrum was determined on the pure liquid with a Perkin-Elmer model 12-C spectrometer modified for double-pass operation. The ultraviolet spectrum was determined in a purified cyclohexane solution with a Beckmann DU spectrophotometer.

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[20] A. A. Pavlic and H. Adkins, *J. Am. Chem. Soc.*, **68**, 1471 (1946).

[21] A. Skita and R. Rossier, *Ber.*, **72**, 265 (1939).

a mixture of diethyl *cis*- and *trans*-hexahydroisophthalate (II) dissolved in 600 ml. of dry ether. After the mixture had been heated under reflux for 48 hr., the excess hydride was decomposed by the addition of 50 ml. of water. The complex was dissolved by the addition of 500 ml. of 10% hydrochloric acid to form a cloudy solution. The aqueous layer was extracted with ether for 11 days in an exhaustive ether extractor. The combined extracts and original ether layer were dried over magnesium sulfate. After the ether had been removed by distillation under reduced pressure, the residue was fractionated through a 10-inch Vigreux column to yield 58.6 g. (94%) of a mixture of *cis*- and *trans*-hexahydroisophthalyl alcohol, b.p. 139° (0.8 mm.), n_D^{25} 1.4879. [Since this work was completed, the preparations of the pure *cis*-hexahydroisophthalyl alcohol, m.p. 55°, and the pure *trans*-hexahydroisophthalyl alcohol, b.p. 112–114° (0.1 mm.), n_D^{24} 1.4941, have been reported[22] starting from the corresponding pure acid in each case.]

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.67; H, 11.11. Found: C, 66.54; H, 10.90

B. From dimethyl hexahydroisophthalate. To a slurry of 105 g. (2.76 moles) of lithium aluminum hydride in 2500 ml. of ether was added dropwise 400 g. (2.0 moles) of a mixture of dimethyl *cis*- and *trans*-hexahydroisophthalate dissolved in 1000 ml. of dry ether. After the reaction mixture had been heated under reflux for 18 hr., the excess hydride was decomposed with 60 ml. of glacial acetic acid and the complex was dissolved with a minimum amount of 10% hydrochloric acid. The aqueous layer was extracted with ether in an exhaustive ether extractor for 6 days. After the combined extracts and original organic layer had been dried over magnesium sulfate, the ether was removed by distillation and the residue was fractionated through a 10-inch Vigreux column to yield 215 g. (75%) of a mixture of *cis*- and *trans*-hexahydroisophthalyl alcohol, b.p. 137–139° (0.8 mm.), n_D^{25} 1.4877.

Hexahydroisophthalyl diacetate (IV). After a mixture of 30 g. (0.21 mole) of a mixture of *cis*- and *trans*-hexahydroisophthalyl alcohol and 1500 ml. of acetic anhydride had been heated under reflux for 48 hr., the excess acetic anhydride and acetic acid were removed by distillation under reduced pressure. The residue was diluted with 100 ml. of ether and the resulting solution was extracted consecutively with water, a saturated solution of sodium carbonate, and a saturated solution of sodium chloride. After the solution had been dried over potassium carbonate, the ether was removed by distillation, and the residue was fractionated through a 10-inch Vigreux column to yield 44 g. (95%) of a mixture of *cis*- and *trans*-hexahydroisophthalyl diacetate (IV), b.p. 94° (0.3 mm.), n_D^{25} 1.4634. [The pure *cis*-hexahydroisophthalyl diacetate, b.p. 105–107° (0.5 mm.), n_D^{15} 1.4598, was recently prepared by a series of involved reactions proceeding through a bicyclic ether.[22]]

Pyrolysis of hexahydroisophthalyl diacetate (IV). At the rate of 36 drops per minute, 166 g. (0.55 mole) of hexahydroisophthalyl diacetate (IV) was added dropwise to a vertical Vycor combustion tube packed with $^1/_{16}$-inch Pyrex helices and heated externally at 555° as described previously.[23] The apparatus was continuously flushed with a slow stream of oxygen-free nitrogen in order to prevent charring. The pyrolyzate, which was collected in a side-inlet flask cooled in a Dry Ice–acetone bath, was extracted with four 100-ml. portions of water. (Titration of an aliquot of the aqueous extracts indicated that 75% of two molar equivalents of acetic acid had been liberated.) After the organic layer had been dried over potassium carbonate, it was fractionated through a 6-inch, helix-packed column to yield 35.8 g. (61%) of 1,3-dimethylenecyclohexane (I), b.p. 122°, n_D^{25} 1.4697; 22 g. (24%) of 1-methylene-2-acetoxymethylcyclohexane (V), b.p. 62° (2.1 mm.), n_D^{25} 1.4600; and 13.9 g. (11% recovery) of unchanged starting ester IV. The yield of the diene I, based on unrecovered IV and V, was 94%.

Anal. Calcd. for C_8H_{12}: C, 88.89; H, 11.11. Found: C, 89.10; H, 11.06.

Calcd. for $C_{10}H_{16}O_2$: C, 71.43; H, 9.52. Found: C, 71.45; H, 9.38.

A sample of the diene I immediately decolorized a solution of bromine in carbon tetrachloride and a dilute potassium permanganate solution. Failure to obtain a precipitate from the attempted reaction with the diene I and maleic anhydride would indicate the absence of any product formed by the rearrangement of both double bonds into conjugation within the ring.

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Acid-Catalyzed Condensation of Phenols and Keto Acids

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Phenol, *o*-cresol, and 2,6-xylenol were condensed with various keto acids or their methyl esters, in the presence of acid catalysts, to form *gem*-bis(*p*-hydroxyphenyl) substituted carboxylic acids.

Extensive investigation of phenol has shown that it acts as a non-specific bactericide and fungicide by denaturing the proteins of the microorganisms. The phenols are often used in conjunction with a wetting agent in order that they may permeate freely, spread evenly, and gain ready access to the infected area. We have undertaken a program to incorporate phenolic groups into aliphatic acids of varying chain length with the hope that germicidal and fungicidal activity may be combined with surface-activating properties.

Phenol, *o*-cresol, and 2,6-xylenol have been condensed with a number of keto acids or their methyl esters to form di-*p*-hydroxyphenyl substituted carboxylic acids.

Concentrated sulfuric acid, 70 per cent sulfuric acid, and hydrogen chloride–acetic acid were the

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