

tane, and then was distilled giving thirteen fractions. Fraction IV, 0.40 g., b.p. 106–107° at 13 mm.,  $[\alpha]^{25D} -8.17^\circ$  (*l* 1, neat), had the highest rotation. The infrared spectrum, by comparison with synthetic mixtures, showed this fraction to contain 70% IV, indicating  $[\alpha]^{25D} -11.7^\circ$ , or 86% of the original rotation. The fractions were combined, and the  $\beta$ -methylvalerophenone was isolated and purified *via* the semicarbazone as described above. Distillation gave 0.5 g. of  $\beta$ -methylvalerophenone, b.p. 124–126° at 13 mm.,  $n^{25D} 1.5089$ ,  $[\alpha]^{25} +0.16^\circ$  (*l* 1, neat). The infrared spectrum of this sample was identical with that of a synthetic mixture.

Another tube was prepared as described above, containing 6.4 g. of IV ( $[\alpha]^{25D} -13.56^\circ$ , *l* 1, neat) and 0.5 g. of diphenylamine, and was heated at 205–215° for 80 minutes. Treatment similar to that described above gave 0.5 g. of  $\beta$ -methylvalerophenone, b.p. 123–125° at 14 mm.,  $[\alpha]^{25D} +0.04^\circ$  (*l* 1, neat).

A third tube was prepared as above, containing 2.62 g. of IV ( $[\alpha]^{25D} -40.00^\circ$ , *l* 1, neat) and 0.22 g. of trinitrobenzene and was heated at 195–205° for 250 minutes. The above procedure was then used, giving 0.45 g. of  $\beta$ -methylvalerophenone, b.p. 110–117° at 10 mm.,  $[\alpha]^{25D} 0.00^\circ$  (*l* 1, neat).

**Study of  $\beta$ -Methylvalerophenone under the Conditions of Rearrangement.**— $\alpha$ -2-Butoxystyrene (1.37 g.), 1.37 g. of  $\beta$ -methylvalerophenone ( $[\alpha]^{25D} +17.50^\circ$ , *l* 1, neat) and 0.05 g. of diphenylamine were put into a tube which was evacuated and sealed. The tube was heated for 155 minutes at 200°. The product was distilled giving 1.58 g. of  $\beta$ -methylvalerophenone, b.p. 129° at 14 mm.,  $[\alpha]^{25D} +9.90^\circ$  (*l* 1, neat),  $n^{25D} 1.5093$ .

**Rearrangement of  $\alpha$ -2-Butoxystyrene in the Presence of Chlororanil.**—Chlororanil (0.05 g.) and 3.05 g. of IV were introduced into a tube, and 2.95 g. of IV was introduced into another tube. The tubes were degassed and sealed. After heating for 57 minutes at 200–210°, the contents were separately distilled at 10 mm. under identical conditions. The tube containing chlororanil gave 2.0 g., b.p. 88–121°, and 0.5 g. of residue; the other gave 2.2 g., b.p. 91–124°, and 0.35 g. of residue. The infrared spectra of both samples were taken, and the two spectra appeared nearly identical.

**Initiation of the Rearrangement of Di-*t*-butyl Peroxide.**— $\alpha$ -2-Butoxystyrene (10 g.) and 1.0 g. of di-*t*-butyl peroxide were introduced into a flask fitted with a total condensation, partial take-off head and a nitrogen supply. The flask was immersed in an oil-bath maintained at 125–135°. As a con-

trol, approximately 1 ml. of  $\alpha$ -2-butoxystyrene was put in a test-tube, and then heated, under nitrogen, in the same oil-bath. Small aliquots were removed from both the control and reaction solutions at 2- to 3-hour intervals, and the infrared spectra were taken. The material which distilled from the reaction mixture was collected in a test-tube immersed in a Dry Ice-acetone-bath. The heating bath was removed after 10.5 hours. Figure 1 shows the catalytic effect of the peroxide. One ml. of distillate was obtained, and it was shown to be predominantly *t*-butyl alcohol by its infrared spectrum. The reaction mixture was distilled giving 5.5 g. of  $\beta$ -methylvalerophenone, b.p. 122–126° at 14 mm.,  $n^{25D} 1.5085$ . A considerable amount of higher boiling residue was also obtained.

**Rearrangement of  $\alpha$ -Phenethoxystyrene.**— $\alpha$ -Phenethoxystyrene (0.98 g.,  $[\alpha]^{25D} +19.58^\circ$ , *l* 0.5, neat) was heated in a sealed evacuated tube at 200° for 180 min. The tube was then cooled and the pale orange solid was recrystallized from 95% ethanol giving 0.95 g. of  $\beta$ -phenylbutyrophenone,  $[\alpha]^{25D} +0.01^\circ$  (*l* 1, *c* 7.90, acetonitrile), m.p. 72.4–73.0°. <sup>24</sup>

**Rearrangement of  $\alpha$ -Neopentoxystyrene (IX).**— $\alpha$ -Neopentoxystyrene (2.4 g.) was heated in a sealed evacuated tube at 230–240° for 420 min. A positive pressure was noted on opening the tube. The product was distilled giving 0.84 g. of material having b.p. 94° at 1 mm.,  $n^{25D} 1.5057$ . The infrared spectrum of this material was identical with that of a synthetic sample of  $\gamma,\gamma$ -dimethylvalerophenone. The 2,4-dinitrophenylhydrazone had m.p. 203–205°, and a mixture of the dinitrophenylhydrazones of the rearranged and synthetic material had m.p. 203–204°.

**The Rate of Rearrangement of  $\alpha$ -2-Butoxystyrene in Heptane.**—A solution of 2.89 g. of IV in heptane (total volume 50.0 ml., *c* 0.328 *M*) was prepared and portions of this solution were added to seven tubes which were evacuated and sealed. They were then heated at 178–179°, and tubes were withdrawn and the contents analyzed at regular intervals. The concentration of the ketone was determined from the infrared spectrum of the solution using a 0.05-mm. fixed cell. A straight line was obtained by plotting the logarithm of the ratio of the intensity of the 8.90  $\mu$  ether band to that of the 8.33  $\mu$  ketone band, against the composition of synthetic mixtures. The concentrations could thus be determined, and the results are shown in Fig. 2.

(24) E. P. Kohler, *Am. Chem. J.*, **31**, 642 (1904), reported m.p. 74°.

SEATTLE 5, WASH.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, WAYNE UNIVERSITY AND THE UNIVERSITY OF MARYLAND]

### Cyclic Dienes. XIII. Substituted 1,2-Dimethylene-4-cyclohexenes<sup>1,2</sup>

BY WILLIAM J. BAILEY,<sup>3</sup> JOSEPH ROSENBERG<sup>4</sup> AND LEWIS J. YOUNG<sup>5</sup>

RECEIVED JULY 21, 1954

Through the pyrolysis of diacetates, 4-methyl-1,2-dimethylene-4-cyclohexene, which is isomeric with pseudocumene, was synthesized in an 89% yield, and 4,5-dimethyl-1,2-dimethylene-4-cyclohexene, which is isomeric with durene, was synthesized in a 77% yield. The structures of these trienes were proved by analysis, ultraviolet absorption and conversion to known derivatives by isomerization and intermediate Diels-Alder adducts.

The pyrolysis of esters has been used in these laboratories to produce in excellent yields and in high purity a series of strained dienes with double bonds exocyclic to five- and six-membered rings.<sup>6–9</sup>

(1) Previous paper in this series, *THIS JOURNAL*, **77**, 1043 (1955).

(2) Presented before the Washington Section of the American Chemical Society, College Park, Md., May, 1952.

(3) Department of Chemistry, University of Maryland, College Park, Md.

(4) Office of Naval Research Fellow, Wayne University, 1950–1951.

(5) Office of Naval Research Fellow, Wayne University, 1949–1950; Atomic Energy Commission Fellow, Wayne University, 1950–1952.

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

(7) W. J. Bailey, J. Rosenberg and L. J. Young, *ibid.*, **76**, 2251 (1954).

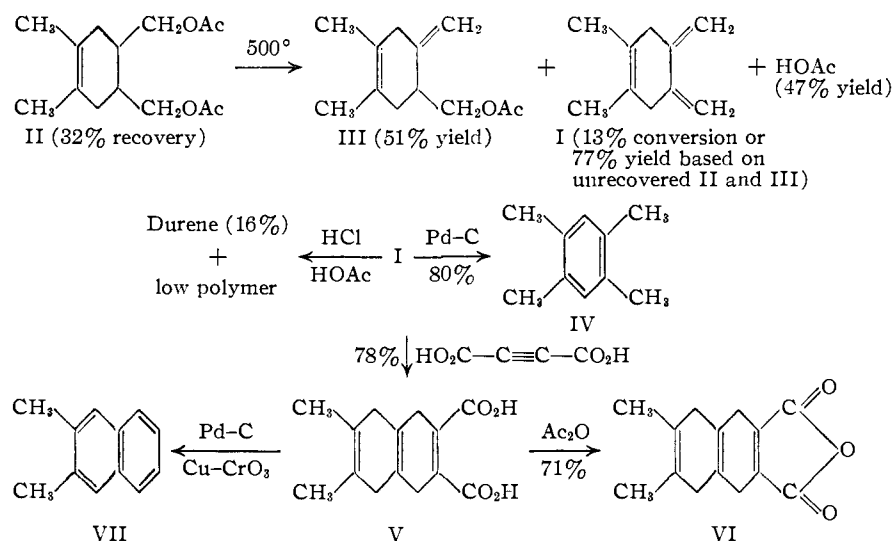
(8) W. J. Bailey and W. R. Sorenson, *ibid.*, **76**, 5421 (1954).

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

In order to determine more exactly the mildness of this synthetic procedure for introducing unsaturation by the pyrolysis of esters, the method was applied to the synthesis of 1,2-dimethylene-4-cyclohexene, which is isomeric with *o*-xylene. It was found that this highly strained triene could be prepared by the pyrolysis of a diacetate in a 92% yield that was completely free of *o*-xylene.<sup>10</sup> Since this synthesis indicated that this pyrolytic method was highly unusual, it was of interest to show that the procedure was general by preparing other isomers of aromatic compounds.

For this reason, the synthesis of 4,5-dimethyl-1,2-dimethylene-4-cyclohexene (I), which is isomeric

(10) W. J. Bailey and J. Rosenberg, *ibid.*, **77**, 73 (1955).



with durene, was undertaken. When 4,5-dimethyl- $\Delta^4$ -tetrahydrophthalyl diacetate (II)<sup>7</sup> was dropped through a Vycor tube packed with glass helices heated at 500°, under such conditions that no carbonization occurred and 47% of the acetic acid was liberated, the triene I was obtained in a 13% conversion. In addition, the intermediate diene monoacetate III was obtained in a 51% yield and 32% of the starting material II was recovered. The yield of triene I, based on unrecovered starting material and diene acetate III, was 77%. If more vigorous pyrolysis conditions were used so that some carbonization occurred, the yield, based on unrecovered material, was lower and some durene and some high boiling polymeric substance were formed.

The structure of the 4,5-dimethyl-1,2-dimethylene-4-cyclohexene (I) was proved by analysis, ultraviolet absorption and conversion to known derivatives. The ultraviolet absorption spectrum did not show either a maximum or a minimum above 220  $m\mu$ , but the  $\epsilon$  rapidly increased as the wave length was lowered and appeared to reach a maximum just below 220  $m\mu$ . The spectrum, therefore, indicated the presence of a pair of conjugated double bonds and the complete absence of any durene (IV).

Treatment of the triene I with hydrochloric acid in acetic acid produced isomerization to durene (IV) in low yield plus a substantial amount of a low molecular weight polymer. Refluxing the triene I in the presence of palladium-on-carbon produced an 80% yield of durene (IV), which did not depress the melting point of an authentic sample.

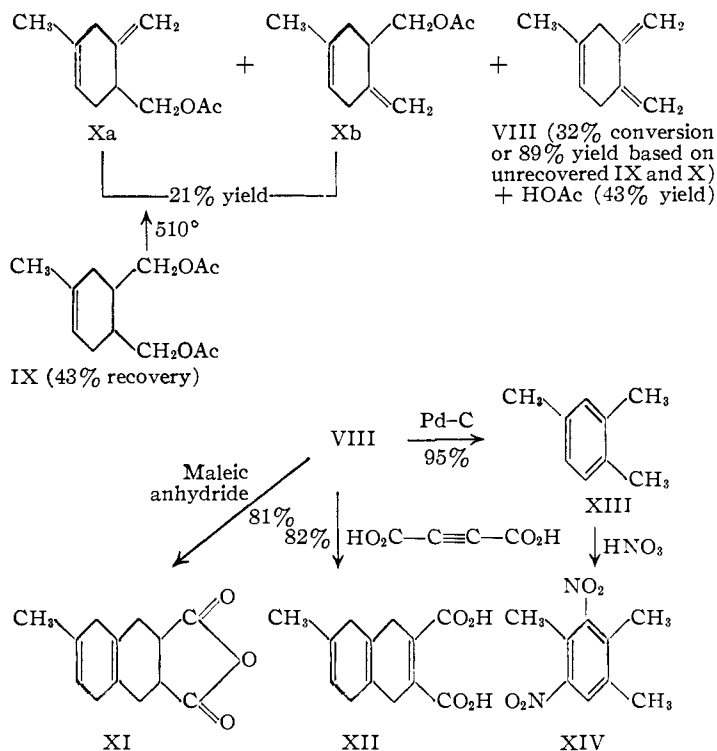
When the triene I was treated with acetylenedicarboxylic acid, the Diels-Alder adduct V was produced in 78% yield. V was difficult to purify since it had a tendency to lose a molecule of water. It therefore was converted to the 6,7-dimethyl-1,4,5,8-tetrahydronaphthalene-2,3-dicarboxylic anhydride (VI). The structure of the adduct V was proved by

simultaneous decarboxylation and dehydrogenation to the known 2,3-dimethylnaphthalene (VII). Mixed melting point with an authentic sample prepared from 4,5-dimethyl-1,2-dimethylenecyclohexane<sup>7</sup> showed no depression.

In a very similar manner, 4-methyl-1,2-dimethylene-4-cyclohexene (VIII), which is isomeric with pseudocumene (XIII), was prepared. When 4-methyl- $\Delta^4$ -tetrahydrophthalyl diacetate (IX)<sup>7</sup> was pyrolyzed at 510°, under such conditions that no carbonization occurred and 43% of the acetic acid was liberated, a 32% conversion to the triene VIII that was completely free of the isomeric pseudocumene was realized. In addition, a 21% yield of a mixture of two isomeric diene monoacetates Xa and Xb plus a 43% recovery of the starting diacetate IX were obtained. The yield of the triene VIII, based on unrecovered starting material and intermediate monoacetate X, was 89%. If more vigorous conditions were used, carbonization took place, lowering the yield and causing isomerization and polymerization.

The structure of the 4-methyl-1,2-dimethylene-4-cyclohexene (VIII) was proved by analysis, ultraviolet absorption, Diels-Alder reactions and isomerization to pseudocumene. The ultraviolet absorption spectrum of the triene VIII did not show a maximum or minimum above 220  $m\mu$  but appeared

conversion to the triene VIII that was completely free of the isomeric pseudocumene was realized. In addition, a 21% yield of a mixture of two isomeric diene monoacetates Xa and Xb plus a 43% recovery of the starting diacetate IX were obtained. The yield of the triene VIII, based on unrecovered starting material and intermediate monoacetate X, was 89%. If more vigorous conditions were used, carbonization took place, lowering the yield and causing isomerization and polymerization.



to reach a maximum  $\epsilon$  just below 220  $m\mu$ , indicating the presence of a conjugated system of double bonds. (1,2-Dimethylenecyclohexane<sup>6</sup> has an  $\epsilon_{\max}$  at 220  $m\mu$ .) The lack of any maximum above 220  $m\mu$  indicates the absence of pseudocumene (XIII).

The presence of the conjugated exocyclic double bonds is further indicated by the fact that VIII reacts readily with maleic anhydride to produce the Diels-Alder adduct XI in an 81% yield and with acetylenedicarboxylic acid to produce the highly unsaturated diacid in an 82% yield.

When 4-methyl-1,2-dimethylene-4-cyclohexene (VIII) was refluxed in the presence of palladium-on-carbon, it isomerized almost completely to pseudocumene (XIII). The pseudocumene was identified by conversion to the solid 3,5-dinitropseudocumene (XIV) and to its solid picrate. Neither of these solid derivatives depressed the melting point of the corresponding authentic sample.

The synthesis of these two highly strained trienes I and VIII in high yields emphasizes that pyrolysis in the vapor state at 500° under conditions adjusted so that no carbonization occurs is much milder than treatment with strong mineral acid at room temperature. It appears likely that many of the examples of low yields and rearranged products that are reported in the literature for the pyrolysis of esters are the result of side reactions catalyzed by the acidic carbon deposit. It is noteworthy that the bulk of the reported successful applications of the pyrolysis of esters have been for preparation of olefins that are not very sensitive to acids or that can also be prepared by an alternative method employing an acid catalyst.

It appears that, if carbonization can be avoided, many other highly strained or sensitive olefins can be prepared by this pyrolytic method.

### Experimental<sup>11</sup>

**4,5-Dimethyl-1,2-dimethylene-4-cyclohexene (I).**—At a rate of 1.5 g. per minute, 331 g. (1.35 moles) of *cis*-4,5-dimethyl- $\Delta^4$ -tetrahydrophthalyl diacetate (II)<sup>7</sup> was dropped through a vertical Vycor pyrolysis tube packed with  $1/16$ -inch Pyrex helices. The tube was externally heated as previously described<sup>8</sup> at a temperature of 500° while a slow stream of oxygen-free nitrogen was passed through. The pyrolysate, which was collected in a flask cooled in Dry Ice, was diluted with ether and the ether solution was extracted several times with water to remove the acetic acid and was dried over sodium carbonate. (Titration of an aliquot portion of the aqueous extracts indicated that 47% of the acetic acid had been liberated.) The ether was removed by distillation and the residue was distilled through a 12-inch, helix-packed column to yield 24.0 g. (18%) of 4,5-dimethyl-1,2-dimethylene-4-cyclohexene (I), b.p. 110–111° (90 mm.),  $n_D^{20}$  1.4977,  $d_4^{20}$  0.8690; 126.2 g. (51%) of 4,5-dimethyl-2-methylene- $\Delta^4$ -tetrahydrobenzyl acetate (III), b.p. 182–184° (90 mm.); and 106.4 g. (32% recovery) of the starting diester II. The yield of triene I, based on unrecovered II and III, was 77%.

*Anal.* Calcd. for  $C_{10}H_{14}$ : C, 89.55; H, 10.45. Found: C, 89.30; H, 10.60.

**Durene (IV).** A. **By Acid Isomerization of 4,5-Dimethyl-1,2-dimethylene-4-cyclohexene (I).**—A mixture of 3.0 g. of 4,5-dimethyl-1,2-dimethylene-4-cyclohexene (I), 25 ml. of glacial acetic acid and three drops of concentrated hydrochloric acid was heated under reflux for 22 hours. Removal of the acetic acid by distillation, followed by recrystallization of the residue from ethanol, yielded 0.5 g. (16%) of

durene (IV), m.p. 79°, plus a low molecular weight polymer. Mixed melting point determination with an authentic sample of durene showed no depression.

B. **By Catalytic Isomerization of 4,5-Dimethyl-1,2-dimethylene-4-cyclohexene (I).**—A mixture of 3.0 g. of 4,5-dimethyl-1,2-dimethylene-4-cyclohexene (I) and 0.5 g. of 5% palladium-on-charcoal was heated under reflux for 22 hours. Recrystallization of the reaction mixture from ethanol, followed by sublimation, yielded 2.4 g. (80%) of durene, m.p. 79°, which did not depress the melting point of an authentic sample of durene.

**6,7-Dimethyl-1,4,5,8-tetrahydronaphthalene-2,3-dicarboxylic Acid (V).**—A solution of 11.4 g. (0.10 mole) of acetylenedicarboxylic acid in 200 ml. of benzene was heated under reflux in a 500-ml., three-necked flask, equipped with a stirrer, a condenser and a dropping funnel. To this mixture was added dropwise with stirring 13.4 g. (0.10 mole) of 4,5-dimethyl-1,2-dimethylene-4-cyclohexene (I) and the mixture was heated for 4 hours. The reaction mixture was cooled and the precipitate was removed by filtration. Two recrystallizations from acetic acid yielded 19.2 g. (78%) of 6,7-dimethyl-1,4,5,8-tetrahydronaphthalene-2,3-dicarboxylic acid (V), m.p. 250–251° dec. V possessed a strong tendency to lose a molecule of water and was, therefore, characterized as the corresponding anhydride VI.

**6,7-Dimethyl-1,4,5,8-tetrahydronaphthalene-2,3-dicarboxylic Anhydride (VI).**—A mixture of 2.0 g. of 6,7-dimethyl-1,4,5,8-tetrahydronaphthalene-2,3-dicarboxylic acid (V), 25 ml. of acetic acid and 5 g. of acetic anhydride was heated under reflux for 1 hour. Cooling of the mixture, followed by recrystallization of the precipitate from acetic acid, yielded 1.3 g. (71%) of 6,7-dimethyl-1,4,5,8-tetrahydronaphthalene-2,3-dicarboxylic anhydride (VI), m.p. 232–233°.

*Anal.* Calcd. for  $C_{14}H_{14}O_3$ : C, 73.02; H, 6.12. Found: C, 73.24; H, 6.19.

**2,3-Dimethylnaphthalene (VII).**—A mixture of 0.2 g. (0.00076 mole) of 6,7-dimethyl-1,4,5,8-tetrahydronaphthalene-2,3-dicarboxylic acid (V), 0.2 g. of 5% palladium-on-carbon and 0.1 g. of copper-chromite catalyst was heated at 290° in a dehydrogenation apparatus<sup>12</sup> until 36.0 ml. (92%) of hydrogen had been collected. During this simultaneous dehydrogenation and decarboxylation, 80 mg. of 2,3-dimethylnaphthalene (VII), m.p. 103–104°, sublimed to the cold finger. VII did not depress the melting point of a sample of 2,3-dimethylnaphthalene prepared previously from 6,7-dimethyl- $\Delta^{2,4a}$ -hexahydronaphthalene-2,3-dicarboxylic acid.<sup>7</sup>

**4-Methyl-1,2-dimethylene-4-cyclohexene (VIII).**—At a rate of 1.0 g. per minute, 70.0 g. (0.29 mole) of *cis*-4-methyl- $\Delta^4$ -tetrahydrophthalyl diacetate (IX)<sup>7</sup> was dropped through the vertical Vycor pyrolysis tube. Optimum recovery of materials was obtained when the tube was externally heated at 510° and conditions were adjusted so that no carbonization occurred on the helices. The pyrolysate, which was collected in a flask cooled in Dry Ice, was diluted with ether and extracted several times with water. (Titration of aliquot portions of the aqueous washings indicated that 43% of the acetic acid had been liberated.) After the organic layer had been dried over magnesium sulfate, the ether was removed by distillation. The residue was fractionated through a 6-inch, helix-packed column to yield 11.0 g. (32%) of 4-methyl-1,2-dimethylene-4-cyclohexene (VIII), b.p. 70° (70 mm.),  $n_D^{20}$  1.4885; 10.9 g. (21%) of a mixture of the two isomeric diene monoacetates Xa and Xb; and 29.9 g. (43% recovery) of the starting diacetate IX. The yield of the triene VIII, based on unrecovered Xa, Xb and starting material IX, was 89%.

*Anal.* Calcd. for  $C_9H_{12}$ : C, 89.93; H, 10.06. Found: C, 90.02; H, 10.27.

**6-Methyl- $\Delta^{6,9}$ -hexahydronaphthalene-2,3-dicarboxylic Anhydride (XI).**—In a 50-ml. erlenmeyer flask were placed 1.9 g. (0.02 mole) of maleic anhydride in 25 ml. of benzene and 2.4 g. (0.02 mole) of 4-methyl-1,2-dimethylene-4-cyclohexene (VIII). As soon as solution had taken place, the reaction mixture spontaneously became warm and a white solid precipitated. After the mixture had been allowed to stand for several hours, the white precipitate was filtered off and washed with ether. Recrystallization of the crude

(11) The authors are indebted to Vivian Kapuscinski, James French and Robert Keen for the analyses. All melting points are corrected.

(12) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath Co., Boston, Mass., 1941, p. 462.

adduct from benzene produced 3.5 g. (81%) of 6-methyl- $\Delta^{6,9(10)}$ -hexahydronaphthalene-2,3-dicarboxylic anhydride (XI), m.p. 132–133.5°.

*Anal.* Calcd. for  $C_{13}H_{14}O_3$ : C, 71.56; H, 6.42; sapon. equiv., 109. Found: C, 71.31; H, 6.28; sapon. equiv., 107.

Acidification of the solution from the determination of the saponification equivalent of XI produced 6-methyl- $\Delta^{6,9(10)}$ -hexahydronaphthalene-2,3-dicarboxylic acid, m.p. 226–228°.

**6-Methyl-1,4,5,8-tetrahydronaphthalene-2,3-dicarboxylic Acid (XII).**—A solution of 2.0 g. (0.02 mole) of acetylenedicarboxylic acid in 25 ml. of benzene was heated under reflux in a 50-ml. flask. To this hot solution was added 2.4 g. (0.02 mole) of 4-methyl-1,2-dimethylene-4-cyclohexene (VIII) and the reaction mixture was heated for 3 hours. The benzene was removed by evaporation and the solid residue was purified by dissolving in a sodium carbonate solution, followed by treatment with charcoal and reprecipitation with dilute hydrochloric acid, to yield 3.5 g. (82%) of 6-methyl-1,4,5,8-tetrahydronaphthalene-2,3-dicarboxylic acid (XII), m.p. 152–153°.

*Anal.* Calcd. for  $C_{13}H_{14}O_4$ : C, 66.66; H, 5.98. Found: C, 66.38; H, 5.76.

**Catalytic Isomerization of 4-Methyl-1,2-dimethylene-4-cyclohexene (VIII).**—A mixture of 3.0 g. (0.025 mole) of 4-

methyl-1,2-dimethylene-4-cyclohexene (VIII) and 0.5 g. of 5% palladium-on-charcoal was heated under reflux for 24 hours. The catalyst was removed by filtration to yield 2.8 g. (93%) of pseudocumene (XIII),  $n_D^{25}$  1.5050. The liquid pseudocumene was identified by conversion to two solid derivatives.

Addition of an alcoholic solution of picric acid to a few drops of the sample of XIII produced a yellow precipitate of pseudocumene picrate, m.p. 95–97° (reported<sup>13</sup> m.p. 97°). A mixed melting point with an authentic sample of pseudocumene picrate also occurred at 95–97°.

A few drops of the sample of pseudocumene was added to a mixture of 1 ml. of fuming nitric acid and 2 ml. of concentrated sulfuric acid. The solution was heated to boiling for 1 minute and then poured into ice-water. The resulting precipitate was removed by filtration and recrystallized from alcohol to yield 3,5-dinitropseudocumene (XIV), m.p. 170–172° (reported m.p.<sup>14</sup> 171–172°). A mixed melting point with an authentic sample of XIV showed no depression.

(13) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 218.

(14) G. Schultz, *Ber.*, **42**, 3607 (1909).

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

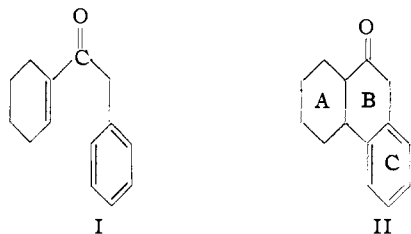
## 12-Alkyloctahydrophenanthrenes Related to Dehydroabiatic Acid

BY WILLIAM E. PARHAM, EDWARD L. WHEELER<sup>1,2</sup> AND R. M. DODSON

RECEIVED APRIL 26, 1954

The synthesis is described of octahydrophenanthrenes with angular alkyl groups at C-12, especially 1,12-dimethyl-1-carboxy-1,2,3,4,9,10,11,12-octahydrophenanthrenes related to dehydroabiatic acid.

Gutsche and Johnson<sup>3</sup> found that when the  $\alpha,\beta$ -unsaturated ketone I was treated with dry hydrogen chloride and aluminum chloride in refluxing benzene,<sup>4</sup> a mixture of *cis*- and *trans*-10-keto-1,2,3,4,9,10,11,12-octahydrophenanthrene (II) was formed in about 5% yield. This paper describes



an extension of this reaction to the synthesis of octahydrophenanthrenes containing angular alkyl groups at C-12, with particular reference to 1,12-dimethyl-1-carboxy-1,2,3,4,9,10,11,12-octahydrophenanthrenes related to dehydroabiatic acid.

The action of formic acid on III, prepared in 68% yield from 2-methylcyclohexanone and phenylacetylene, gave a liquid ketone (IV) in 68% yield. The ultraviolet spectrum of this ketone showed a maximum in agreement with that calcu-

lated<sup>5</sup> for IV, but a molar extinction coefficient of one-half that of I. The ultraviolet spectrum of the semicarbazone of IV showed a pronounced hump on the benzenoid absorption, and there was a point of inflection between 233 and 240  $m\mu$ . By subtracting the absorption due to the benzene ring, an estimated maximum at 240  $m\mu$  ( $\epsilon$  10,000) was obtained. These results agree closely with the data reported by Turner and Voitle<sup>6</sup> for 1-acetylcyclohexene and 2-methyl-1-acetylcyclohexene, and there can be little doubt that the same explanation obtains for these two cases. Absorption due to the carbonyl group in I is found at 1670  $cm^{-1}$ . In IV the carbonyl band is at 1690  $cm^{-1}$ , with a hump at 1705  $cm^{-1}$ , indicating that a small amount of the unconjugated  $\beta,\gamma$ -unsaturated ketone was present.<sup>6</sup> In view of the steric hindrance in IV, the observed shift in carbonyl absorption in the infrared spectrum is consistent with the interpretation given for the ultraviolet spectrum.<sup>6</sup> A single semicarbazone was obtained from IV, which is further

(1) From the Ph.D. Thesis of Edward L. Wheeler, University of Minnesota, 1953.

(2) Parke, Davis Fellow, 1952–1953. Part of this work was sponsored by the Greater University Fund of the University of Minnesota.

(3) C. D. Gutsche and W. S. Johnson, *THIS JOURNAL*, **68**, 2239 (1946).

(4) These conditions are not those normally employed for the Bogert–Cook reaction.

(5) R. B. Woodward, *THIS JOURNAL*, **63**, 1123 (1941); **64**, 76 (1952).

(6) R. B. Turner and D. M. Voitle, *ibid.*, **73**, 1403 (1951).