

**Reactions of 1,1-Pentamethylene-*as*-hydrindacene: A. Oxidation.**—The hydrocarbon (0.5 g.) was heated in a sealed tube at 190° for twenty hours with nitric acid (5 ml.) and water (10 ml.). The aqueous solution was evaporated to dryness and the residue treated with excess diazomethane in ether. The ether was distilled and the solid methyl ester recrystallized from methanol; m. p. 129.8–130.4°. The melting point of a mixture of this product and an authentic sample<sup>20</sup> of methyl mellophanate was 130.0–130.8°.

**B. Dehydrogenations.**—The hydrocarbon (0.5 g.) mixed with 15% palladium-on-charcoal (0.1 g.) was heated slowly to 340° and kept at this temperature for eight hours. During this time 150 ml. (75%) of hydrogen was evolved. By extraction with boiling ethanol 0.1 g. of the original hydrocarbon was recovered. The main product was a dark tarry material insoluble in ethanol and soluble in benzene which did not sublime at 200° under 0.1 mm. pressure. Other dehydrogenation reagents, sulfur, selenium, palladium black and chloranil<sup>21</sup> also produced mixtures of starting material and unidentifiable polymeric substances in varying amounts.

**C. Reaction with N-Bromosuccinimide.**—The hydrocarbon (0.5 g.) was refluxed with N-bromosuccinimide (1.42 g.) and benzoyl peroxide (0.02 g.) in carbon tetrachloride (20 ml.) for two hours. There was no evolution of hydrogen bromide during the first part of the reaction and the solution remained nearly colorless. Small amounts of hydrogen bromide were evolved toward the end of the reaction when most of the N-bromosuccinimide had been converted to succinimide. Potassium acetate (1 g.) was added and refluxing continued for an additional two hours. Processing of the reaction mixture produced only a viscous brown oil which gave a positive test for bromine with alcoholic silver nitrate.

**13-Methyl-1,2-cyclopentano-5,6,7,8,9,10,13,14-octahydrophenanthrene.**—2-Methylcyclohexanone (7.9 g.) was added dropwise to the Grignard reagent prepared from magnesium (1.7 g.) and  $\beta$ -4-hydrindenylethyl bromide (15.8 g.) in dry ether (300 ml.). After refluxing for one-half hour the mixture was decomposed with ammonium chloride solution and the product extracted with ether. The ether extract was washed with water, dried and the ether removed. The residual alcohol was distilled; there

was obtained 10 g. (58%) of material which boiled at 158–162° (0.07 mm.). The distillate was stirred at –5° with 90% sulfuric acid (28 ml.) for one hour and then at room temperature for an additional hour. When isolated as above there was obtained 7 g. (78%) of the hydrocarbon which boiled at 136–139° (0.3 mm.);  $n_D^{25}$  1.5674.

*Anal.* Calcd. for  $C_{18}H_{24}$ : C, 89.94; H, 10.06. Found: C, 89.87; H, 9.85.

In one experiment processing of the alcohol with subsequent distillation gave a substance which boiled at 128–142° (0.1 mm.). This must have been the olefin resulting from dehydration of the expected alcohol because cyclization with sulfuric acid as above gave the same product as from the alcohol.

This hydrocarbon was allowed to stand in the refrigerator for six months, but remained as a viscous uncrystallizable oil. Oxidation with dilute nitric acid as in the previous case also produced mellophanic acid. Dehydrogenation with ether selenium at 340° for twenty hours or with palladium-on-charcoal at 250–300° for three hours produced cyclopentanophenanthrene (40–60% yield); m. p. 131–133°. The picrate of the dehydrogenation product melted at 132–134°.<sup>22</sup>

The trinitrobenzene adduct melted at 164.8–165.8° and the trinitrotoluene adduct melted at 100.0–100.8°.<sup>22</sup>

### Summary

A convenient method for the preparation of 4-chlorohydrindene has been described.

A synthesis for cyclopentanophenanthrene derivatives has been illustrated by the conversion of 4-chlorohydrindene to 13-methyloctahydrocyclopentanophenanthrene.

It has been observed that in the absence of the methyl group this synthetic procedure leads to a spirane, 1,1-pentamethylene-*as*-hydrindacene.

The structural evidence and a possible mechanism of formation has been discussed for those two hydrocarbons.

(22) Ruzicka, Ehmman, Goldberg and Hosli, *Helv. Chim. Acta*, **16**, 833 (1933).

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(20) This sample was kindly furnished by Prof. L. I. Smith; see Smith and Carlson, *THIS JOURNAL*, **61**, 288 (1939).

(21) Arnold and Collins, *ibid.*, **61**, 1407 (1939).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

## Pinacols Derived from the Xylenols

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Although many investigators studied the pinacol reduction,<sup>2,3,4</sup> a review of the literature indicates that the pinacol reduction has not been applied to dimethylhydroxypropiophenones. It is the aim of this investigation to present the synthesis of 3,4-hexanediols. The phenols used for starting materials were 2,5-dimethylphenol, 3,5-dimethylphenol, 2,4-dimethylphenol, and 2,6-dimethylphenol.

The hydroxypropiophenones required for the pinacol reduction were obtained in the following

(1) Present address: Wallace & Tiernan Products, Inc., Belleville 9, New Jersey.

(2) K. Sisido and H. Nozaki, *THIS JOURNAL*, **70**, 776 (1948).

(3) M. S. Newman, *ibid.*, **62**, 1683 (1940).

(4) E. Adler, G. J. Gie and H. von Euler, Swedish Patent 115,816, February 12, 1946; C. A., **41**, 486 (1947).

manner. Flynn and Robertson<sup>5</sup> converted 4-hydroxy-1,3-dimethylbenzene to the propionate and then by the Fries rearrangement, with anhydrous aluminum chloride in the absence of a solvent, obtained 3,5-dimethyl-2-hydroxypropiophenone. By heating one mole of 3,5-dimethylphenyl propionate with one mole of anhydrous aluminum chloride at 120–125° for five hours, Baddeley<sup>6</sup> isolated 2,4-dimethyl-6-hydroxypropiophenone. If two moles of anhydrous aluminum chloride are heated with one mole of 3,5-dimethylphenyl propionate at the same temperature, there is a shift of one of the methyl groups thus producing 4,5-dimethyl-2-hydroxypropiophenone.<sup>6</sup> The 3,5-dimethyl-4-hy-

(5) D. G. Flynn and A. Robertson, *J. Chem. Soc.*, 215 (1936).

(6) G. Baddeley, *J. Chem. Soc.*, 273 (1943).

droxypropiofenone needed for the pinacol reduction was prepared from 1,3-dimethyl-2-amino-benzene by first diazotizing the amine to the 2,6-dimethylphenol by the method of Bamberger.<sup>7</sup> This was converted to the 2,6-dimethylphenyl propionate which by the Fries rearrangement, with anhydrous aluminum chloride in dry nitrobenzene at room temperature, yielded the desired 3,5-dimethyl-4-hydroxypropiofenone. Niederl and Weiss<sup>8</sup> synthesized 2,5-dimethyl-4-hydroxypropiofenone by esterifying 2,5-dimethylphenol with propionyl chloride and converting the propionate to the hydroxypropiofenone by means of anhydrous aluminum chloride in dry nitrobenzene at room temperature.

The pinacol reduction was carried out by adding the dimethylhydroxypropiofenone in moist ether to freshly prepared aluminum amalgam.<sup>9</sup> The time required for effecting reaction was at least twenty-four hours, and the dark brown gummy residues isolated from the reduction gave low yields of the desired products on crystallization. From the appearance of the gummy residue, it was obvious that much decomposition had occurred and that it was probably due to the presence of the free hydroxyl groups. To avoid this, the hydroxyl groups were esterified and then subjected to the pinacol reduction. When this reaction was carried out in moist ether, no better yields were realized. By performing the reduction in moist ethyl acetate,<sup>10</sup> better yields of the pinacol diacetate were obtained, and the time required for the reaction was decreased to one and one-half hours. In contrast to this the moist ether method required a minimum of twenty-four hours. The course of the reaction in the moist ethyl acetate method was followed exclusively by the change in temperature. The reaction was continued until the temperature reached a maximum and then decreased by 5°. By using this method, most of the decomposition previously encountered was eliminated.

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

**2,6-Dimethylphenyl Propionate (I).**—To 20 g. (0.16 mole) of 2,6-dimethylphenol dissolved in 200 ml. of dry benzene was added dropwise 30 g. (0.32 mole) of propionyl chloride, and the reaction mixture was refluxed for three hours. The cooled reaction mixture was poured into an ice water mixture, and the benzene layer was washed successively with several portions of water, 5% cold potassium hydroxide solution, and finally with water. The benzene phase was dried over anhydrous sodium sulfate, filtered, and the solvent removed by distillation. The red oily residue was distilled under vacuum; b. p. 112–113° (16 mm.); yield 21.8 g.

*Anal.* Calcd. for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>: C, 74.15; H, 7.86. Found: C, 74.01; H, 7.98.

Saponification of 2,6-dimethylphenyl propionate was effected with alcoholic potassium hydroxide thus yielding

(7) E. Bamberger, *Ber.*, **36**, II, 2036 (1903).

(8) J. B. Niederl and P. Weiss, *This Journal*, **70**, 2894 (1948).

(9) E. C. Dodds, L. Goldberg, W. Lawson and R. Robinson, *Proc. Roy. Soc. (London)*, **B127**, 140 (1939).

(10) V. Niederl, C. A. Siconolfi, A. Bloom and C. T. VanMeter, *This Journal*, **70**, 509 (1948).

(11) Melting points and boiling points given are uncorrected.

2,6-dimethylphenol; m. p. 45.5–47°. Mixed melting point with an authentic sample of 2,6-dimethylphenol showed no depression of melting point.

**3,5-Dimethyl-4-hydroxypropiofenone (II).**—Twenty-seven grams (0.15 mole) of 2,6-dimethylphenyl propionate was dissolved in 135 ml. of dry nitrobenzene. After cooling the solution in an ice-bath, 24 g. of anhydrous aluminum chloride was added in small portions to the reaction mixture. The reaction was set aside at room temperature for a minimum of twenty-four hours. The green solution was poured into an ice-water mixture, and then acidified with dilute hydrochloric acid. The hydrolyzed aluminum chloride complex was extracted with ether, and the combined nitrobenzene-ether extracts were extracted with 10% sodium hydroxide. After washing with several portions of ether to remove traces of nitrobenzene, the alkaline solution was acidified with dilute hydrochloric acid to yield the crude solid. Recrystallization from dilute methanol yielded 18.9 g. of 3,5-dimethyl-4-hydroxypropiofenone; m. p. 106–107°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>: C, 74.15; H, 7.86. Found: C, 74.19; H, 7.99.

**3,5-Dimethyl-4-propionoxypropiofenone (III).**—Following the procedure outlined for I, 6.5 g. (0.03 mole) of 3,5-dimethyl-4-hydroxypropiofenone was treated with 9.2 g. (0.1 mole) of propionyl chloride and the mixture was refluxed for three hours. By fractional distillation *in vacuo*, 7.0 g. of the desired ester was obtained; b. p. 144–145° (2.6 mm.).

*Anal.* Calcd. for C<sub>14</sub>H<sub>18</sub>O<sub>3</sub>: C, 71.79; H, 7.69. Found: C, 71.93; H, 7.69.

**2,4-Dimethyl-6-acetoxypropiofenone (IV).**—Twenty-one grams (0.11 mole) of 2,4-dimethyl-6-hydroxypropiofenone<sup>6</sup> was refluxed for two hours with 20 g. (0.19 mole) of acetic anhydride using pyridine as a catalyst. The ester was isolated as described under I; b. p. 171–172° (16 mm.); yield 15 g.

*Anal.* Calcd. for C<sub>13</sub>H<sub>16</sub>O<sub>3</sub>: C, 70.90; H, 7.27. Found: C, 70.68; H, 7.43.

**4,5-Dimethyl-2-acetoxypropiofenone (V).**—By refluxing 42 g. (0.23 mole) of 4,5-dimethyl-2-hydroxypropiofenone<sup>6</sup> with 30 g. (0.29 mole) of acetic anhydride and a few drops of pyridine, 41 g. of V was obtained; b. p. 180–182° (25 mm.).

*Anal.* Calcd. for C<sub>13</sub>H<sub>16</sub>O<sub>3</sub>: C, 70.90; H, 7.27. Found: C, 70.61; H, 7.44.

**3,4-bis-(6'-Hydroxy-2',4'-dimethylphenyl)-3,4-hexanediol (VI).**—Twelve grams of aluminum foil was cut into strips, crumpled loosely, amalgamated with mercuric chloride, and successively washed with water, ethanol and ether. The aluminum amalgam thus prepared was then covered with 500 ml. of moist ether, and to the reaction mixture was added 10 g. (0.056 mole) of 2,4-dimethyl-6-hydroxypropiofenone.<sup>6</sup> The reaction mixture was set aside for twenty-four hours, and then filtered. The viscous residue was extracted with several portions of ether and the ether extracts were combined with the filtrate. This was dried over anhydrous sodium sulfate, filtered, and concentrated by removing the solvent by distillation. The gummy residue, which was crystallized from ethanol, yielded 2.1 g. of a white crystalline solid; m. p. 177–178°.

*Anal.* Calcd. for C<sub>22</sub>H<sub>30</sub>O<sub>4</sub>: C, 73.74; H, 8.37; mol. wt., 358. Found: C, 73.57; H, 8.62; mol. wt., 343.

**3,4-bis-(2'-Hydroxy-3',5'-dimethylphenyl)-3,4-hexanediol (VII).**—Following the procedure outlined for VI, 10 g. (0.056 mole) of 3,5-dimethyl-2-hydroxypropiofenone<sup>6</sup> yielded 1.7 g. of the crude 3,4-hexanediol. One and four tenths grams of pure VII was obtained by recrystallization from ethyl alcohol; m. p. 196–197°.

*Anal.* Calcd. for C<sub>22</sub>H<sub>30</sub>O<sub>4</sub>: C, 73.74; H, 8.37; mol. wt., 358. Found: C, 73.65; H, 8.39; mol. wt., 349.

**3,4-bis-(2'-Hydroxy-4',5'-dimethylphenyl)-3,4-hexanediol (VIII).**—Twenty grams (0.11 mole) of 4,5-dimethyl-2-hydroxypropiofenone<sup>6</sup> was treated with 25 g.

of the freshly prepared aluminum amalgam in moist ether. The reaction mixture was set aside for forty-eight hours and then worked up in a similar manner as described in VI. Crystallization and recrystallization from methanol yielded 1.1 g. of VIII; m. p. 185-187°.

*Anal.* Calcd. for  $C_{22}H_{30}O_4$ : C, 73.74; H, 8.37; mol. wt., 358. Found: C, 73.47; H, 8.59; mol. wt., 354.

**3,4-bis-(3',5'-Dimethyl-4'-hydroxyphenyl)-3,4-hexanediol (IX).**—From 7 g. (0.039 mole) of 3,5-dimethyl-4-hydroxypropiophenone and 10 g. of aluminum amalgam in moist ether was obtained 0.5 g. of IX. The product was recrystallized from 80% ethanol; m. p. 202-203.5°.

*Anal.* Calcd. for  $C_{22}H_{30}O_4$ : C, 73.73; H, 8.37; mol. wt., 358. Found: C, 73.54; H, 8.51; mol. wt., 341.

**3,4-bis-(2',5'-Dimethyl-4'-hydroxyphenyl)-3,4-hexanediol, (X).**—Ten grams (0.056 mole) of 2,5-dimethyl-4-hydroxypropiophenone<sup>8</sup> was treated with 12 g. of aluminum amalgam in moist ether in a similar manner as described in VI. From the dark brown gummy residue, by crystallization from ethanol, was obtained 0.6 g. of X; m. p. 212-214°.

*Anal.* Calcd. for  $C_{22}H_{30}O_4$ : C, 73.73; H, 8.37; mol. wt., 358. Found: C, 73.59; H, 8.62; mol. wt., 339.

**3,4-bis-(3',5'-Dimethyl-4'-propionoxyphenyl)-3,4-hexanediol (XI).**—Six grams (0.025 mole) of 3,5-dimethyl-4-propionoxypropiophenone was dissolved in 100 ml. of moist ethyl acetate and to this solution was added amalgamated aluminum which was freshly prepared from 12 g. of cut aluminum foil. The course of the reaction was followed exclusively by the change in temperature, and the reaction was allowed to continue until the temperature rise reached a maximum and then decreased by 5°. The actual change in temperature amounted to 39°, and the time required to complete the pinacol reduction was one and one-half hours. After filtering the viscous reaction mixture, the residual aluminum amalgam was washed with several portions of ethyl acetate. The combined ethyl acetate fractions were dried over anhydrous magnesium sulfate, filtered and the solvent removed by distillation. The gummy residue was crystallized by adding a small amount of low boiling petroleum ether. A white crystalline product was obtained by washing the crude solid with cold benzene; m. p. 171-173°; yield 2.4 g.

*Anal.* Calcd. for  $C_{28}H_{38}O_6$ : C, 71.49; H, 8.08; mol. wt., 470. Found: C, 71.31; H, 8.31; mol. wt., 454.

Saponification of 3,4-bis-(3',5'-dimethyl-4'-propionoxyphenyl)-3,4-hexanediol with alcoholic potassium hydroxide yielded 3,4-bis-(3',5'-dimethyl-4'-hydroxyphenyl)-3,4-hexanediol; m. p. 202-203°. Mixed melting point of this dihydroxyhexanediol with a sample of IX showed no depression in the melting point.

**3,4-bis-(6'-Acetoxy-2',4'-dimethylphenyl)-3,4-hexanediol (XII).**—Following the procedure outlined for XI, 15 g. (0.068 mole) of 2,4-dimethyl-6-acetoxypropiophenone in

300 ml. of moist ethyl acetate was treated with aluminum amalgam to yield 5.9 g. of the desired pinacol diacetate; m. p. 161-162°.

*Anal.* Calcd. for  $C_{26}H_{34}O_6$ : C, 70.58; H, 7.69; mol. wt., 442. Found: C, 70.41; H, 7.87; mol. wt., 438.

Refluxing XII with alcoholic potassium hydroxide yielded 3,4-bis-(6'-hydroxy-2',4'-dimethylphenyl)-3,4-hexanediol; m. p. 177°. Mixed melting point of this with a sample of VI produced no depression in the melting point.

**3,4-bis-(2'-Acetoxy-4',5'-dimethylphenyl)-3,4-hexanediol (XIII).**—Twelve grams (0.054 mole) of 4,5-dimethyl-2-acetoxypropiophenone was dissolved in 250 ml. of moist ethyl acetate, and this solution was treated with freshly prepared aluminum amalgam. The esterified hexanediol was isolated as described under XI; m. p. 168-170°; yield 3.9 g.

*Anal.* Calcd. for  $C_{26}H_{34}O_6$ : C, 70.58; H, 7.69; mol. wt., 442. Found: C, 70.31; H, 7.91; mol. wt., 429.

Hydrolysis of the pinacol diacetate (XIII) with alcoholic potassium hydroxide yielded the corresponding dihydroxyhexanediol; m. p. 186°. This isolated dihydroxyhexanediol when mixed with a sample of VIII showed no depression in the melting point.

**3,4-bis-(2'-Acetoxy-3',5'-dimethylphenyl)-3,4-hexanediol (XIV).**—From 9 g. (0.04 mole) of 3,5-dimethyl-2-acetoxypropiophenone in 125 ml. of moist ethyl acetate, using the method outlined under XI, was obtained 4.1 g. of the crude 3,4-hexanediol. Trituration with cold petroleum ether (30-60°) yielded 3.6 g. of pure 3,4-bis-(2'-acetoxy-3',5'-dimethylphenyl)-3,4-hexanediol; m. p. 178-180°.

*Anal.* Calcd. for  $C_{26}H_{34}O_6$ : C, 70.58; H, 7.69; mol. wt., 442. Found: C, 70.53; H, 7.82; mol. wt., 431.

The pinacol diacetate (XIV) was converted to 3,4-bis-(2'-hydroxy-3',5'-dimethylphenyl)-3,4-hexanediol by gently refluxing with alcoholic potassium hydroxide; m. p. 197°. Mixed melting point with an authentic sample of VII showed no depression in melting point.

### Summary

The preparation of 3,4-hexanediols from dimethyl hydroxypropiophenones is described. The low yields obtained in this pinacol reduction have been improved by first esterifying the dimethylhydroxypropiophenones and then effecting the pinacol reduction with aluminum amalgam in moist ethyl acetate. The use of moist ethyl acetate resulted in increased yields, decreased reaction time and decreased decomposition during the course of the reaction.

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