2. The change in the pseudo first order constant with percentage sulfuric acid follows changes expected for oxonium ion concentration, taking into consideration the formation of the carbonyl ion, $(CH_3)_3C_6H_2CO^+$. From this it can be concluded that the probable rate-controlling step is the reaction between the conjugate acid of mesitoic acid and water.

3. The decarboxylation of methyl mesitoate in strong sulfuric acid was shown to proceed by way of intermediate hydrolysis to mesitoic acid.

RECEIVED FEBRUARY 2, 1949

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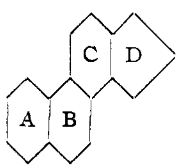
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

# The Use of 4-Substituted Hydrindenes in the Preparation of Cyclopentanophenanthrene Derivatives[1]

BY RODERICK A. BARNES[2] AND LOUIS GORDON[3]

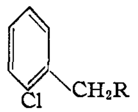
The synthesis of substances having the cyclopentanophenanthrene nucleus has usually been carried out by building up rings C and D starting with a substituted benzene or naphthalene.



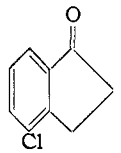
The alternate approach involving construction of rings A and B from a hydrindene derivative has not been previously employed.[4] The 5-substituted hydrindenes which are the major products of the usual aromatic substitution reactions on hydrindene could cyclize in either of two ways.[5] In the present work this alternate approach has been applied by starting with 4-substituted hydridenes, which can cyclize only at the desired position.

The starting material 4-chlorohydrindene[6] was most conveniently prepared in large quantity from *o*-chlorotoluene.

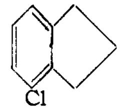
The conversion of I to the *o*-chlorobenzyl halides (II, III) was effected by bromine, N-bromosuccinimide, and sulfuryl chloride in 98, 82 and 76% yields, respectively.[7] The reaction of sodiomalonic ester with either II or III produced the desired ester (IV) in 76% yield; in addition there was isolated a crystalline by-product, m. p. 79°, which is believed to be the dialkylation product, ethyl di-(*o*-chlorobenzyl)-malonate. The acid (V) was produced in nearly quantitative yield by refluxing IV with a mixture of acetic and hydrochloric acids. The cyclization of V to 4-chloro-1-hydrindone (VI) and subsequent reduction to VII were carried out according to the method of Fieser and Hershberg.[6] Catalytic reduction of the ketone (VI) with platinum and hydrogen also produced VII in good yield; however, the chlorine atom was hydrogenolyzed if the reduction was allowed to proceed after the theoretical amount of hydrogen had been absorbed. The over-all yield of 4-chlorohydrindene (VII) by this procedure was 55%.



I, R = H
II, R = Br
III, R = Cl
IV, R = $CH(COOEt)_2$
V, R = $CH_2COOH$

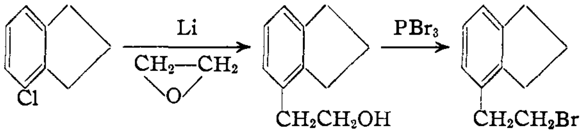


VI



VII

In order to build up rings A and B of the cyclopentanophenanthrene nucleus a tertiary alcohol was prepared which could then be cyclized as in Bardhan–Sengupta phenanthrene synthesis.[8]



VII VIII IX

The reaction of 4-hydrindenyl lithium with ethylene oxide takes place more readily and in better yield (82%) than is usually the case with analogous Grignard reagents; this is undoubtedly due

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[1] Presented in part at the New York meeting of the A. C. S., September, 1947.

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[3] Submitted in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, Department of Chemistry, Columbia University, June, 1948.

[4] By analogy with some natural steroids it might be anticipated that an aromatic ring C would be difficult to reduce to the perhydro system.

[5] The cyclization of γ-5-hydrindenylbutyric acid yields only the linear ketone, 5,6,7,8-tetrahydrobenz[f]indanone-5, Sengupta, *J. Ind. Chem. Soc.*, **16**, 89 (1939).

[6] Fieser and Hershberg, THIS JOURNAL, **59**, 394 (1937), have prepared this substance in ca. 45% over-all yield from *o*-chlorobenzaldehyde.

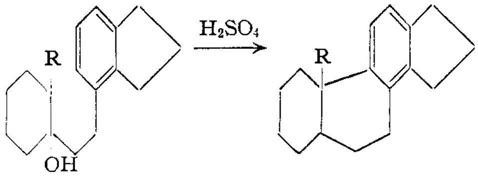
[7] *o*-Chlorobenzyl chloride is now commercially available.

[8] This general method for preparation of the phenanthrene ring system was first described by Bardhan and Sengupta, *J. Chem. Soc.*, 2520 (1932), and was later elaborated by others; (a) Cook and Hewett, *ibid.*, 1098 (1933); (b) Perlman, Davidson and Bogert, *J. Org. Chem.*, **1**, 288 (1936); (c) Kon, *J. Chem. Soc.*, 1081 (1933).

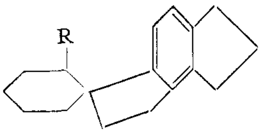
to the fact that no stable coördination complex is formed by interaction of lithium with the oxide as is the case with magnesium.

In the reaction of the Grignard reagent from 4-β-hydrindenylethyl bromide (IX) with cyclohexanone or 2-methylcyclohexanone, there was always formed in addition to the desired tertiary alcohols (X, XI) small amounts of a crystalline hydrocarbon $C_{22}H_{26}$ (m. p. 83°) which is believed to be the coupling product 1,4-di-4′-hydrindenylbutane. The tertiary alcohols could not be obtained analytically pure, some dehydration took place even when they were distilled at 0.2 mm. pressure.

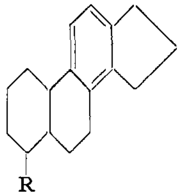
The cyclodehydration of alcohols X and XI could produce two kinds of cyclization products,[9] either cyclopentanophenanthrenes and/or spiranes.



X, R = H XI, R = $CH_3$ XII, R = H XIII, R = $CH_3$



XIV, R = H XV, R = $CH_3$



XVI, R = $CH_3$

By analogy with previously studied cases[10] it would be predicted that X would yield largely the cyclopentanophenanthrene (XII) accompanied by small amounts of spirane (XIV) while XI would produce almost exclusively the desired hydrocarbon (XIII).

On the basis of the experimental evidence available[11] we have assigned the spirane structure XIV to the cyclization product of alcohol X and the octahydrocyclopentanophenanthrene structure XIII to the product from XI. The spirane XIV (in contrast to the corresponding phenanthrene XII) can exist in only a single stereoisomeric form and this cyclization product was isolated as a crystalline solid (m. p. 72.6–73.6°) in 55–60% yield.[12] Attempted dehydrogenation of this solid substance with selenium, sulfur, palladium black, palladium-on-charcoal and chloranil failed to yield any detectable amount of cyclopentanophenanthrene. Furthermore, reaction of this material with N-bromosuccinimide was slow and hydrogen bromide was evolved in small amount only when the reaction was nearly completed.[13]

In contrast to the spirane XIV the cyclization product of alcohol XI was a liquid which could not be induced to crystallize. This hydrocarbon was dehydrogenated by both selenium and palladium-on-charcoal smoothly and under comparatively mild conditions to produce cyclopentanophenanthrene.[14]

The identity of the dehydrogenated product with cyclopentanophenanthrene was demonstrated by the melting point of the hydrocarbon itself and three derivatives, the picrate, the trinitrobenzene adduct and the trinitrotoluene adduct. It is possible to distinguish cyclopentanophenanthrene and 9-methylcyclopentanophenanthrene by these derivatives, therefore we believe that the unknown 8-methylcyclopentanophenanthrene and hence structure XVI can also be eliminated by these observations.

The cyclization of alcohols X and XI is believed to occur by primary formation of the corresponding carbonium ions, which in the presence of the sulfuric acid catalyst enter into the following equilibrium. This same equilibrium mixture of carbonium ions can be formed by reaction of sulfuric acid with the olefins corresponding to the tertiary alcohols.

On the basis of the simple idea that a tertiary carbonium ion is more stable than a secondary and hence present in greater concentration, it would be predicted that when R = H a spirane should be the major product. When R = $CH_3$ it could be predicted only that the cyclopentanophenanthrene XVI derived from ion XVIII is much less likely than the other two possibilities, spirane XV and cyclopentanophenanthrene XIII. Thus, the structures proposed for our cyclization products are in agreement with the predictions of this simplified concept of the reaction mechanism. A more accurate description of the mechanism would require some knowledge of the rate of transformation of one carbonium ion to another and the rate of reaction of the ions with the aromatic nucleus.

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[9] In both cases the products were shown to be cyclization products and not open chain isomers by oxidation with dilute nitric acid to mellophanic acid (1,2,3,4-tetracarboxybenzene).

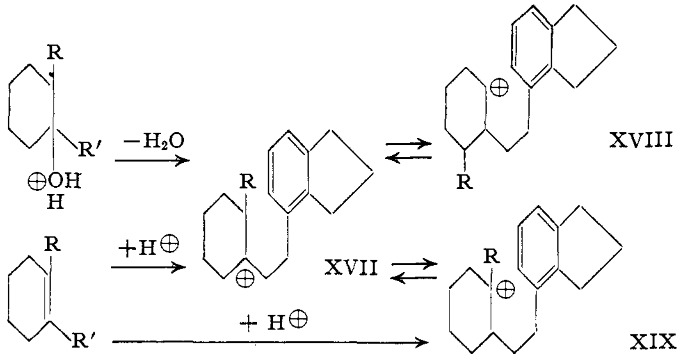
[10] The cyclization of 1-β-phenylethyl-1-cyclohexanol has been found by Perlman, Davidson and Bogert, ref. 8b, to yield approximately 14% of spirane and 86% of octahydrophenanthrene. The cyclization product of 2-methyl-1-β-phenylethyl-1-cyclohexanol has been assigned the phenanthrene structure; however, the only experimental evidence for this assignment is the dehydrogenation to phenanthrene.

[11] Unequivocal syntheses designed to prove conclusively the structures of these two cyclization products are now in progress.

[12] This is not conclusive support for the spirane structure, since Cook, McGinnis and Mitchell, *J. Chem. Soc.*, 286 (1944), have found that the aluminum chloride cyclization of 1-β-phenylethyl-1-cyclohexene yielded *cis as*-octahydrophenanthrene as the major product. Small amounts of the *trans* isomer and the spirane were also formed.

[13] This is interpreted as evidence in favor of the spirane structure because of observations in our Laboratories that compounds having the structure $Ar-CH_2CH_2R$ react as above with N-bromosuccinimide while substances with structures $Ar-CHR-CHR_2$ react rapidly and exothermically with immediate and vigorous evolution of hydrogen bromide: Barnes, THIS JOURNAL, **70**, 145 (1948), Barnes and Buckwalter, unpublished results. The alternate cyclopentanophenanthrene structure XII for the solid cyclization product falls into this second classification.

[14] Although some spiranes are dehydrogenated only under more drastic conditions than this product or not at all, the observed dehydrogenation does not eliminate the spirane structure XV from further consideration. Cook and Hewett, *J. Chem. Soc.*, 365 (1934); Cook, Hewett and Robinson, *ibid.*, 169 (1939).



## Experimental[15]

*o*-**Chlorobenzyl Bromide.**—A. Freshly distilled *o*-chlorotoluene (63 g.) was refluxed for two and one-half hours with N-bromosuccinimide (44 g.) and carbon tetrachloride (30 ml.). The succinimide which crystallized at the surface of the liquid was filtered off and the residue was fractionated. There was obtained 42 g. (82%) of product which boiled at 103–107° (12 mm.).[16]

B. Bromine (128 g.) was added over a period of two hours to refluxing *o*-chlorotoluene (95 g.) which was mechanically stirred and illuminated with a 150-watt lamp. The reaction was complete after an additional three hours of heating and illumination. On distillation there was obtained 152 g. (98%) of the bromide.[17] A portion of this bromide reacted with potassium *o*-nitrophenolate to produce the expected ether, m. p. 83–84°.[18]

*o*-**Chlorobenzyl Chloride.**—*o*-Chlorotoluene (81 g.) was refluxed for three hours with sulfuryl chloride (72 g.) and benzoyl peroxide (0.7 g.). The product was washed with water, dried and distilled; there was obtained 65 g. (76%) of the chloride which boiled at 82–84% (9 mm.).[19]

**Diethyl** *o*-**Chlorobenzylmalonate.**—Diethyl malonate (420 g.) was added rapidly to a cold (10°) solution of sodium (46 g.) dissolved in absolute ethanol (1 liter) and the solution stirred for one-half hour. *o*-Chlorobenzyl halide (2 moles) was added from a dropping funnel as rapidly as possible without allowing the temperature to rise above 5°. When the addition was complete the mixture was stirred at 10° for two hours, then allowed to warm to room temperature and finally refluxed for one hour. The excess alcohol was distilled on the steam-bath; the residue was treated with water and processed in the usual manner. On distillation there was obtained 433 g. (76%) of the monoalkylated malonic ester which boiled at 155–160° (4 mm.).

*Anal.* Calcd. for $C_{14}H_{17}O_4Cl$: C, 59.05; H, 6.02; Cl, 12.45. Found: C, 58.98; H, 5.86; Cl, 12.65.

The distillation residue crystallized on standing and after recrystallization from ethanol there was obtained 27 g. of material which melted at 79°. This is presumed to be ethyl di-(*o*-chlorobenzyl)-malonate.

*Anal.* Calcd. for $C_{21}H_{22}O_4Cl_2$: C, 61.62; H, 5.42; Cl, 17.33. Found: C, 61.52; H, 5.52; Cl, 17.41.

This preparation was also carried out in absolute methanol as the solvent. The dimethyl ester instead of the diethyl ester was the main product (*ca.* 70% yield); b. p. 104° (0.15 mm.).

*Anal.* Calcd. for $C_{12}H_{13}O_4Cl$: C, 56.15; H, 5.11; Cl, 13.81. Found: C, 56.07; H, 5.14; Cl, 13.86.

The dialkylation product in this case melted at 93° (from methanol).

*Anal.* Calcd. for $C_{19}H_{18}O_4Cl_2$: C, 59.85; H, 4.76; Cl, 18.60. Found: C, 59.82; H, 4.80; Cl, 18.66.

β-**2-Chlorophenylpropionic Acid.**—Diethyl *o*-chlorobenzylmalonate (1120 g.) was refluxed with concentrated hydrochloric acid (3 liters) and acetic acid (200 ml.) for twenty-seven hours. An additional liter of concentrated hydrochloric acid was added in three portions during the reflux period. On cooling the acid crystallized; it was filtered and recrystallized from benzene and petroleum ether. There was obtained 691 g. (95%) of product which melted at 96–97°.[6]

**4-Chloro-1-hydrindone.**—This preparation was carried out according to the method of Fieser and Hershberg.[6] β-2-Chloropropionic acid (100 g.) produced 106 g. (96%) of the acid chloride which boiled at 126–129° (12 mm.). Cyclization of the acid chloride yielded 78 g. (90%) of the ketone which melted at 89–90°.

**4-Chlorohydrindene.**—A solution of 4-chloro-1-hydrindone (30 g.) in alcohol (400 ml.) was shaken with hydrogen (40 lb. pressure) and platinum oxide (0.3 g.) until the calculated amount of hydrogen had been absorbed. The catalyst was removed and the solution fractionated to yield 22 g. (80%) of product which boiled at 92–94° (12 mm.).[6]

*Anal.* Calcd. for $C_9H_9Cl$: C, 70.82; H, 5.90. Found: C, 71.06; H, 6.00.

The Clemmensen reduction[6] of 4-chloro-1-hydrindone also produced the desired product (85% yield).

β-**4-Hydrindenylethanol.**—4-Chlorohydrindene (71 g.) was dropped into a refluxing mixture of lithium (13 g.) and dry ether (800 ml.). The reaction mixture was stirred vigorously and refluxed for six hours. Ethylene oxide was passed into the cooled solution which was then allowed to stand overnight. When the reaction mixture was treated with water and processed in the usual manner, there was obtained 62 g. (82%) of product which boiled at 141–146° (8 mm.).

*Anal.* Calcd. for $C_{11}H_{14}O$: C, 81.43; H, 8.70. Found: C, 81.30; H, 8.21.

β-**4-Hydrindenylethyl Bromide.**—β-4-Hydrindenylethanol (62 g.) dissolved in dry benzene (100 ml.) was cooled to 5° and phosphorus tribromide (70 g.) in benzene (50 ml.) was added. The mixture was stirred overnight, then poured onto ice. After processing there was obtained 62 g. (72%) of the bromide which boiled at 141–148° (11 mm.).

*Anal.* Calcd. for $C_{11}H_{13}Br$: C, 58.67; H, 5.82. Found: C, 58.79; H, 6.02.

**1,1-Pentamethylene-*as*-hydrindacene.**—Cyclohexanone (11 g.) was added dropwise at 0° to the Grignard reagent prepared from magnesium (2.7 g.) and β-4-hydrindenylethyl bromide (25 g.) in dry ether (500 ml.). After stirring for one-half hour the reaction mixture was decomposed with ice and dilute hydrochloric acid. Upon processing the reaction mixture and distillation of the crude alcohol there was obtained 22 g. (83%) of material which boiled at 175–180° (2 mm.); b. p. 158° (0.7 mm.). The residue from this distillation solidified and after recrystallization from petroleum ether melted at 83°.

*Anal.* Calcd. for $C_{22}H_{26}$: C, 90.97; H, 9.03. Found: C, 90.63; H, 9.03.

The partially dehydrated alcohol obtained above (20 g.) was cyclized by stirring with 90% sulfuric acid (84 ml.) at −5° for two hours; the product was extracted with petroleum ether. The petroleum ether solution was washed with cold concentrated sulfuric acid, water and sodium bicarbonate solution. Evaporation of the petroleum ether yielded 11 g. (59%) of a crystalline product which melted at *ca.* 68°. The pure sublimed hydrocarbon melted at 72.6–73.6°.

*Anal.* Calcd. for $C_{17}H_{22}$: C, 90.20; H, 9.80. Found: C, 90.0; H, 9.62.

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[15] All melting points are corrected. Microanalyses are by Lois E. May.

[16] Shoesmith and Slater, *J. Chem. Soc.*, 219 (1926).

[17] This procedure was based on the preparation of *p*-bromobenzyl bromide described by Weizmann and Patai, THIS JOURNAL, **68**, 150 (1946).

[18] Lasch, *Monatsh.*, **34**, 1662 (1913).

[19] Meisenheimer, Zimmermann and Kummer, *Ann.*, **446**, 225 (1925).

**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[20] 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[21] 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 β-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.); $n^{25}$D 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°.[22]

The trinitrobenzene adduct melted at 164.8–165.8° and the trinitrotoluene adduct melted at 100.0–100.8°.[22]

## 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.

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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).

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

NEW YORK, N. Y. RECEIVED OCTOBER 18, 1948

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

# Pinacols Derived from the Xylenols

BY PHILIP WEISS[1] AND JOSEPH B. NIEDERL

Although many investigators studied the pinacol reduction,[2,3,4] 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 manner. Flynn and Robertson[5] 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[6] 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.[6] The 3,5-dimethyl-4-hy-

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[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).

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

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