541. *The Synthesis of Some New Phenols.*

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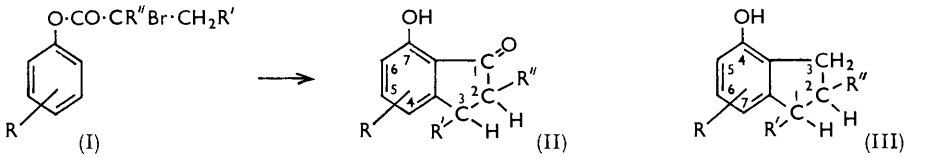
2-Ethyl-3-methyl- and 3-ethyl-2-methyl-phenol, 1-, 2-, 5-, 6-, and 7-methylindan-4-ol and 1- and 4-methylindan-5-ol have been prepared for the first time. An improved synthesis of 6-methylindan-5-ol is also described.

In a recent analytical investigation of a sample of coal-tar phenols, a number of constituents not hitherto reported in the literature were isolated.[1] The syntheses now described were carried out to assist in their identification.

Ethylmethylphenols are major components of the fraction of coal-tar acids boiling at 225—240°, and of the ten possible isomers only the 2-ethyl-3-methyl- and 3-ethyl-2-methyl-phenol had not previously been described. The first has now been prepared fairly simply from 2-bromo-3-methylphenol by Grignard replacement of the bromine by an ethyl radical after protection of the hydroxyl group by methylation. Hydrolysis then gave the required phenol.

The route adopted for preparation of the 3-ethyl-2-methyl isomer required 3-hydroxy-2-methylbenzoic acid as starting material. Fieser and Lothrop [2] had obtained this acid by caustic fusion of sodium 3-aminonaphthalene-1,5-disulphonate and reported their 18—27% yields as a considerable improvement over those quoted by Perkin and Baudisch [3] who used the same method. The yield has now been increased to 76% by using the acid sodium salt and carrying out the fusion in an atmosphere of nitrogen. The substituted



(a) R = Me (*ortho* to OH), R′ = R″ = H. (b) R = Me (*meta* to OH), R′ = R″ = H. (c) R = Me (*para* to OH), R = R′ = H. (d) R = R″ = H, R′ = Me. (e) R = R′ = H, R″ = Me.

benzoic acid was then converted into the acetophenone by passing it admixed with acetic acid over thoria, as described by Senderens [4] for production of 2-methylacetophenone from *o*-toluic acid. Clemmensen reduction of this gave 3-ethyl-2-methylphenol. By the same reactions 3-methoxy-2-methylbenzoic acid gave the corresponding anisole and thence the phenol on hydrolysis. This compound was shown to be identical with a 2,3-substituted ethylmethylphenol isolated from tar.

The fraction of tar acids boiling at 250—280° was found to consist essentially of alkylindanols, mainly the monomethyl derivatives. The predominance of this type of structure was largely unsuspected, it having been supposed that this range of tar acids would simply consist of more highly substituted homologues of phenol. Of the six possible methylindan-4-ols all except the 1- and the 2-isomer have been found and of the six methylindan-5-ols only the 2-derivative has not been identified in tar. All the methylindan-4-ols except the 3-isomer have now been prepared for the first time, in addition to 1- and 4-methylindan-5-ol. An improved synthesis of 6-methylindan-5-ol is also described.

Reduction of the corresponding 7-hydroxy-methylindan-1-ones (II) offered the most convenient means of obtaining all the methylindan-4-ols except the 3-methyl isomer. The indanones were obtained from suitably substituted phenyl α-bromo-propionates or -butyrates (I) by treatment with aluminium chloride under conditions favouring a Fries rearrangement of the acyl radical to the position *ortho* to the hydroxyl group, followed by

[1] Dean, White, and McNeil, *J. Appl. Chem.*, 1959, **9**, 629.
[2] Fieser and Lothrop, *J. Amer. Chem. Soc.*, 1936, **58**, 749.
[3] Perkin and Baudisch, *J.*, 1909, **95**, 1883.
[4] Senderens, *Compt. rend.*, 1911, **152**, 90.

heating to bring about ring closure. 5-, 6-, and 7-Methylindan-4-ol (IIIa, b, and c) were obtained by starting from α-bromopropionyl bromide and *o*-, *m*-, and *p*-cresol respectively; reaction of phenol with α-bromobutyryl bromide and with α-bromo-α-methylpropionyl bromide, followed by treatment with aluminium chloride, yielded the 1- and the 2-isomers (IIId and e). The yields of the combined rearrangement and cyclization stage tended to be rather low, about 40%, but the final conversion of indanones into indanols by Clemmensen reduction was generally satisfactory.

The products obtained were in general the result of *ortho*-rearrangements. In one experiment with *o*-tolyl α-bromopropionate under different conditions and at a lower temperature, a small quantity of 4-methylindan-5-ol was eventually isolated; presumably this had been formed by a *para*-shift of the acyl group, giving 5-hydroxy-4-methylindan-1-one as the intermediate compound. It might have been expected that in this instance ring closure would have occurred on the less hindered side of the benzene ring to give 5-hydroxy-6-methylindan-1-one, yielding on reduction 6-methylindan-5-ol.

Two unsuccessful attempts were made to synthesize 3-methylindan-4-ol. In the first it was intended to convert 7-methoxyindan-1-one into 4-methoxy-3-methylindene by treatment with methylmagnesium iodide followed by dehydration. This on hydrogenation and hydrolysis should then have given the required indanol. Attempts to hydrogenate the crude dehydration product gave complex products in which no detectable amounts of 4-methoxy-3-methylindane could be found by infrared examination. This failure was somewhat unexpected as syntheses of substituted 1-methylindanes from the corresponding indan-1-ones by this method have been reported.[5] The second route was analogous to that successfully applied in the preparation of 1-methylindan-5-ol. It was hoped to cyclize β-*o*-methoxyphenylbutyric acid to give 4-methoxy-3-methylindan-1-one which on reduction and hydrolysis should give 3-methylindan-4-ol. The acid was obtained in quantitative yield by the reduction of 2-methoxy-β-methylcinnamic acid, prepared by a Reformatsky reaction on 2-methoxyacetophenone, but attempts at ring closure failed.

It had previously been suggested that although cyclizations can take place *meta*- to an *ortho-para*-directing group, a powerful group such as methoxyl has a definite deactivating effect.[6] Thus β-*p*-methoxyphenylpropionic acid with hydrofluoric acid is reported as giving only 3% of 6-methoxyindan-1-one, whereas the unsubstituted β-phenylpropionic acid gives 77% of indan-1-one. Although this might indicate that cyclization is difficult at a position *meta* to a methoxyl group, this would appear to depend largely on the reagent used, since use of aluminium chloride in the above reaction with β-*p*-methoxyphenylpropionic acid increases the yield to 86%. Further, as described below, in the synthesis of 1-methylindan-5-ol 29% cyclization to a position *meta* to a methoxy-group occurs in the Friedel–Crafts ring closure of β-*p*-methoxyphenylbutyric acid.

1-Methylindan-5-ol was obtained by a 5-stage sequence from 4-methoxyacetophenone. This was converted by a Reformatsky reaction into 4-methoxy-β-methylcinnamic acid which was then reduced to the corresponding butyric acid. The acid chloride of this was cyclised with aluminium chloride to 6-methoxy-3-methylindan-1-one which on Clemmensen reduction followed by demethylation gave 1-methylindan-5-ol.

6-Methylindan-5-ol has been prepared by Fieser and Lothrop [7] in an 8-step synthesis starting from *p*-tolualdehyde. A much shorter route now devised takes advantage of the production of 6-bromoindan-5-ol in good yield directly from indan-5-ol. This was converted into a methoxyindane and a methyl group introduced by a Grignard reaction. 6-Methylindan-5-ol was then obtained by hydrolysis. The yield was rather low and the crude product contained some indan-5-ol which may have arisen by loss of the methyl group during hydrolysis or incomplete replacement of all the bromine at the previous stage.

[5] Elsner and Parker, *J.*, 1957, 592.
[6] Johnson, " Organic Reactions," John Wiley and Sons, Inc., New York. 4th edn.. Vol. II, pp. 120, 157.
[7] Fieser and Lothrop, *J. Amer. Chem. Soc.*, 1936, **58**, 2052.

4-Methylindan-5-ol was prepared by a similar sequence from 4-bromoindan-5-ol. The latter had previously been made by Hunsberger *et al.*,[8] by bromination of 6-hydroxyindane-5-carboxylic acid followed by decarboxylation. Butylation of indan-5-ol proceeds exclusively in the 6-position and, as the t-butyl group can be both readily introduced and removed, this substituent was preferred to the carboxyl group for blocking the active 6-position before bromination.

Experimental

2-Bromo-3-methylanisole.—This was obtained by the action of dimethyl sulphate (6·7 g.) on an alkaline solution of 2-bromo-3-methylphenol[9] (10 g.). 2-Bromo-3-methylanisole (7·3 g., 68%) had m. p. 42° [from light petroleum (b. p. 60—80°)] (lit.,[10] 41·5—42°).

2-Ethyl-3-methylanisole.—A solution of 2-bromo-3-methylanisole (9·1 g.) in dry ether (50 ml.) was poured on to magnesium turnings (1·2 g.) during 15 min. The mixture was maintained under reflux for a further hour, then cooled and a solution of diethyl sulphate (14·0 g.) in dry ether (30 ml.) was added during 15 min. A vigorous reaction occurred with deposition of a white precipitate. After being heated for 1 hr. the mixture was cooled and poured into ice (60 g.) and 2N-hydrochloric acid (75 ml.). The product obtained by extraction with ether was dissolved in light petroleum (b. p. 60—80°) and chromatographed on alumina, to give an almost quantitative yield of crude 2-ethyl-3-methylanisole (6·9 g., n_D^{25} 1·504).

2-Ethyl-3-methylphenol.—A solution of the crude anisole (6·9 g.) in acetic acid (50 ml.), 57% hydriodic acid (6 ml.), and 60% hydrobromic acid (10 ml.) was heated under reflux for 4 hr. in an atmosphere of carbon dioxide. The bulk of the acetic acid was removed by distillation and the residue neutralised with aqueous sodium carbonate and then extracted with ether. The ethereal solution was in turn extracted with 10% sodium hydroxide solution, and the phenol recovered from the alkaline solution by acidification with hydrochloric acid and extraction with ether. The crude phenolic material (2·1 g.) was chromatographed in light petroleum (b. p. 60—80°) on silica gel. The main fraction (1·0 g., 16%) was a low-melting solid which crystallised from light petroleum (b. p. 60—80°) to give *2-ethyl-3-methylphenol* as needles, m. p. 27·5° (Found: C, 79·6; H, 9·0. $C_9H_{12}O$ requires C, 79·4; H, 8·9%); the *phenylurethane* had m. p. 162° (Found: N, 5·4. $C_{16}H_{17}NO_2$ requires N, 5·5%).

3-Hydroxy-2-methylbenzoic Acid.—Sodium hydrogen 3-aminonaphthalene-1,5-disulphonate (100 g.) was heated in an autoclave with sodium hydroxide (200 g.) in water (200 ml.) for 12 hr. at 275—280° under an initial nitrogen pressure of 40 atm. The product was dissolved in water (charcoal), the solution was filtered and acidified, and the precipitated hydroxy-methylbenzoic acid filtered off. Further quantities of the acid were recovered by extracting the mother-liquors with ether, and purified by dissolution in aqueous sodium carbonate, washing with ether, and precipitation with acid. 3-Hydroxy-2-methylbenzoic acid crystallised from water in needles (35·5 g., 76%), m. p. 145—146° (lit.,[2] 141—142°).

3-Methoxy-2-methylbenzoic Acid.—The acid was converted into the methyl ester of the methoxy-derivative in 83% yield by treatment with dimethyl sulphate. The liquid product was hydrolysed quantitatively with 20% aqueous potassium hydroxide to 3-methoxy-2-methylbenzoic acid, m. p. 152° (from methanol) (Found: C, 64·9; H, 6·2%; equiv., 166. Calc. for $C_9H_{10}O_3$: C, 65·05; H, 6·1%; equiv., 166·2). Fieser and Lothrop [2] give m. p. 145—146°.

3-Hydroxy-2-methylacetophenone.—A solution of 3-hydroxy-2-methylbenzoic acid (10 g.) in hot acetic acid (30 ml.) was passed over a pelleted thoria catalyst (50 ml.) at 470—480° during 4 hr. After an ethereal solution of the product had been washed with aqueous sodium carbonate, the solvent was removed to give *3-hydroxy-2-methylacetophenone* (3·2 g., 32%), m. p. 121° (from ethanol) (Found: C, 71·8; H, 6·8. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%).

3-Methoxy-2-methylacetophenone.—Similar treatment of 3-methoxy-2-methylbenzoic acid (8·35 g.) gave *3-methoxy-2-methylacetophenone* (7·1 g.) as an oil. This was purified by elution with light petroleum (b. p. 40—60°) through a column of alumina deactivated with methanol (Found: C, 73·5; H, 7·5. $C_{10}H_{12}O_2$ requires C, 73·1; H, 7·4%).

3-Ethyl-2-methylanisole.—3-Methoxy-2-methylacetophenone (1·01 g.) was heated under

[8] Hunsberger, Lednicer, Gutowsky, Bunker, and Taussig, *J. Amer. Chem. Soc.*, 1955, **77**, 2466.
[9] Huston and Petersen, *J. Amer. Chem. Soc.*, 1933, **55**, 3879.
[10] Benkeser and Buting, *J. Amer. Chem. Soc.*, 1952, **74**, 3011.

reflux with amalgamated zinc and dilute hydrochloric acid for 10 hr. Extraction with light petroleum (b. p. 40—60°) afforded 3-ethyl-2-methylanisole (0·73 g.) as an oil. This was not purified before demethylation.

3-Ethyl-2-methylphenol.—(a) *From 3-hydroxy-2-methylacetophenone.* The acetophenone (1·48 g.) was reduced as above during 3½ hr. to give *3-ethyl-2-methylphenol* (0·52 g., 39%) as white needles, m. p. 68°.

(b) *From 3-ethyl-2-methylanisole.* (i) The crude anisole (0·73 g.) was heated under reflux with hydriodic acid (5 ml.; *d* 1·7) for 3½ hr., then diluted with water and extracted with light petroleum. The extract was washed with 10% aqueous sodium hydroxide, and the alkaline solution acidified after washing with light petroleum. 3-Ethyl-2-methylphenol (0·24 g., 36%), m. p. 67°, was recovered from the acidic solution by extraction with light petroleum.

(ii) A solution of the anisole (3·75 g.) in benzene (25 ml.) was added to one of aluminium bromide (19 g.) in the same solvent (120 ml.). After being kept overnight the mixture was heated under reflux for 14 hr., then added to water. The benzene phase was washed with water and extracted with 10% aqueous sodium hydroxide. 3-Ethyl-2-methylphenol (0·95 g., 28%) was obtained as needles, m. p. 68°, from a petroleum extract of the acidified aqueous solution.

The m. p.s of the three samples of the phenol were not depressed on admixture with each other. Recrystallization from light petroleum raised the m. p. to 71·5° (Found: C, 79·5; H, 8·9. $C_9H_{12}O$ requires C, 79·4; H, 8·9%). The phenol gave *3-ethyl-2-methylphenoxyacetic acid*, m. p. 161° (Found: C, 68·0; H, 7·1%; equiv., 186. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·3%; equiv., 194), and an *α-naphthylurethane*, m. p. 120° (Found: N, 4·6. $C_{20}H_{19}NO_2$ requires N, 4·6%), *4-biphenylylurethane*, m. p. 196° (Found: N, 4·3. $C_{22}H_{21}NO_2$ requires N, 4·2%), and *p-nitrobenzoate*, m. p. 181° (Found: N, 4·9. $C_{16}H_{15}NO_4$ requires N, 4·9%).

7-Hydroxymethylindan-1-ones.—The *o-*, *m-*, and *p*-tolyl esters [11] (15 g.) of α-bromopropionic acid were each treated with aluminium chloride (30 g.) at room temperature without cooling, then heated for 4 hr. at 150—160°. The mixtures were cooled and decomposed with ice and hydrochloric acid. The tarry products were steam-distilled, the indanones crystallising from the distillates. *7-Hydroxy-6-methylindan-1-one* (3·5 g., 35%), from *o*-tolyl α-bromopropionate, was collected as needles, m. p. 80—81·5° (Found: C, 73·7; H, 6·2. $C_{10}H_{10}O_2$ requires C, 74·05; H, 6·2%); it gave an intense blue colour with ferric chloride and its *2,4-dinitrophenylhydrazone* had m. p. 301—303° (Found: N, 16·2. $C_{16}H_{14}N_4O_5$ requires N, 16·4%). *7-Hydroxy-5-methylindan-1-one* (4·0 g., 40%), from *m*-tolyl α-bromopropionate, crystallised as needles, m. p. 123·5—125° (Found: C, 73·8; H, 6·1. $C_{10}H_{10}O_2$ requires C, 74·05; H, 6·2%). 7-Hydroxy-4-methylindan-1-one (4·3 g., 43%), from *p*-tolyl α-bromopropionate, was also obtained as needles, m. p. 112·5—114° (lit.,[12] 110°).

The rearrangement of phenyl α-bromobutyrate (15 g.) was done in a slightly different manner.[13] After the treatment with aluminium chloride (35 g.) and heating for 4 hr. at 130° the solid product was decomposed and steam-distilled as before. The oil which separated from the distillate was extracted with ether and washed with aqueous sodium carbonate and water. Removal of the solvent left 7-hydroxy-3-methylindan-1-one (5·4 g., 54%) as an oil (Conover [13] gives b. p. 63°/0·07 mm., n_D^{20} 1·5635). It formed a 2,4-dinitrophenylhydrazone, m. p. 263—264° (lit.,[12] 256°).

A modification of a method described by Bruce *et al.*[14] was used for the rearrangement and cyclization of phenyl α-bromo-α-methylpropionate (25 g.). This was added dropwise to a melt of powdered aluminium chloride (55 g.) and sodium chloride (11 g.) at 140°. On completion of the addition the temperature was raised to 180° for 5 min. and the product worked up as for the 7-hydroxy-3-isomer above, to give *7-hydroxy-2-methylindan-1-one* (5·4 g., 36%) also as an oil; it was purified by washing its almost insoluble sodium salt (Found: C, 74·1; H, 6·3%).

5-Hydroxy-4-methylindan-1-one.—*o*-Tolyl α-bromopropionate (44·8 g.) was treated with aluminium chloride (44·8 g.) in carbon disulphide (50 ml.).[15] After decomposition with hydrochloric acid the product was steam-distilled and the residue washed with ether. The extract

[11] Bischoff, *Ber.*, 1892, **25**, 1308.
[12] Hayes and Thomson, *J.*, 1956, 1585.
[13] Conover, *J. Amer. Chem. Soc.*, 1953, **75**, 4017.
[14] Bruce, Sorrie, and Thomson, *J.*, 1953, 2403.
[15] Blatt, " Organic Reactions," John Wiley and Sons, Inc., New York, 4th edn., Vol. I, p. 342.

was washed with aqueous sodium hydroxide, and the alkaline solution acidified with hydrochloric acid and extracted with light petroleum. The dried extract was chromatographed on silica, to give crude 5-hydroxy-4-methylindan-1-one (7·7 g.).

Methylindanols.—The crude indanones (5·4 g.) were heated under reflux for 3 hr. with amalgamated zinc (10 g.) and 6N-hydrochloric acid (50 ml.). The products were washed with ether, and the phenols removed with 10% sodium hydroxide solution. After acidification the phenols were recovered by ether-extraction and crystallised from light petroleum (b. p. 40—60°). The following were thus prepared.

1-*Methylindan*-4-*ol* (2·2 g., 45%), m. p. 56—57° (Found: C, 80·9; H, 8·3. $C_{10}H_{12}O$ requires C, 81·0; H, 8·2%) [4-*biphenylylurethane*, m. p. 193° (Found: N, 4·2. $C_{23}H_{21}NO_2$ requires N, 4·1%)].

2-*Methylindan*-4-*ol* (3·75 g., 76%), m. p. 48—49° (Found: C, 80·8; H, 8·3. $C_{10}H_{12}O$ requires C, 81·0; H, 8·2%) [4-*biphenylylurethane*, m. p. 153° (Found: N, 4·3. $C_{23}H_{21}NO_2$ requires N, 4·1%)].

5-*Methylindan*-4-*ol*, (4·45 g., 90%), m. p. 100° (Found: C, 80·8; H, 8·2. $C_{10}H_{12}O$ requires C, 81·0; H, 8·2%) [*phenylurethane*, m. p. 144° (Found: N, 5·3. $C_{17}H_{17}NO_2$ requires N, 5·2%); α-*naphthylurethane*, m. p. 207° (Found: N, 4·3. $C_{21}H_{19}NO_2$ requires N, 4·4%); p-*nitrobenzoate*, m. p. 182° (Found: N, 4·7. $C_{17}H_{15}NO_4$ requires N, 4·7%); 3,5-*dinitrobenzoate*, m. p. 140° (Found: N, 8·3. $C_{17}H_{14}N_2O_6$ requires N, 8·2%)].

6-*Methylindan*-4-*ol* (4·4 g., 89%), m. p. 81·5—83° (Found: C, 81·0; H, 8·3. $C_{10}H_{12}O$ requires C, 81·0; H, 8·2%) [*aryloxyacetic acid*, m. p. 159° (Found: C, 70·3; H, 6·7%; equiv., 201. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%; equiv., 206); *phenylurethane*, m. p. 136° (Found: N, 5·3. $C_{17}H_{17}NO_2$ requires N, 5·2%); α-*naphthylurethane*, m. p. 165° (Found: N, 4·4. $C_{21}H_{19}NO_2$ requires N, 4·4%); 4-*biphenylylurethane*, m. p. 158° (Found: N, 4·1. $C_{23}H_{21}NO_2$ requires N, 4·1%); p-*nitrobenzoate*, m. p. 102° (Found: N, 4·6. $C_{17}H_{15}NO_4$ requires N, 4·7%); 3,5-*dinitrobenzoate*, m. p. 135° (Found: N, 8·4. $C_{17}H_{14}N_2O_6$ requires N, 8·2%)].

7-*Methylindan*-4-*ol* (3·4 g., 69%), m. p. 85·5—87° (Found: C, 81·0; H, 8·2. $C_{10}H_{12}O$ requires C, 81·0; H, 8·2%) [*phenylurethane*, m. p. 123° (Found: N, 5·3. $C_{17}H_{17}NO_2$ requires N, 5·2%); α-*naphthylurethane*, m. p. 144° (Found: N, 4·6. $C_{21}H_{19}NO_2$ requires N, 4·4%); 3,5-*dinitrobenzoate*, m. p. 165° (Found: N, 8·0. $C_{17}H_{14}N_2O_6$ requires N, 8·2%)].

4-Methylindan-5-ol (0·92 g., 19%), m. p. 97·5—98·0° undepressed on admixture with the specimen prepared by the alternative route described below.

β-o-*Methoxyphenylbutyric Acid.*—2-Methoxy-β-methylcinnamic acid,[16] m. p. 96—97° (32·1 g.), prepared by a Reformatsky reaction between 2-methoxyacetophenone and ethyl bromoacetate, was treated in 2% aqueous sodium hydroxide (500 ml.) with 3% sodium amalgam (650 g.) during 30 min. Then the mixture was heated to, and kept at, 70° for 24 hr. The aqueous phase was decanted, acidified with hydrochloric acid, and extracted with ether. Removal of the solvent gave a quantitative yield of the *butyric acid* which on crystallization from light petroleum (b. p. 60—80°) had m. p. 48—50° (Found: C, 68·2; H, 7·2. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·3%).

Attempts to cyclise this acid were made by: heating the acid chloride with aluminium chloride in carbon disulphide; heating the acid with phosphorus pentoxide at 120° for 2 hr.; treating the acid with 40% hydrofluoric acid at room temperature for 24 hr.; treating the acid with anhydrous hydrogen fluoride at 0° for 1 hr. and then allowing the fluoride to evaporate during 4 hr. at room temperature; and adding the acid to a fused melt of aluminium chloride and sodium chloride at 140° and then raising the temperature to 180° for 5 min.[14] Only unchanged material was recovered from the 40% acid; the other methods yielded unidentifiable oils. Only the last product showed evidence of ring closure on infrared examination and as it resisted reduction by both the Clemmensen and the Wolff–Kischner method, it was concluded that it was not the desired product.

β-p-*Methoxyphenylbutyric Acid.*—4-Methoxy-β-methylcinnamic acid, m. p. 155—156°, prepared by a Reformatsky reaction as above, was reduced quantitatively with sodium amalgam as above. β-p-*Methoxyphenylbutyric acid* (Found: C, 68·1; H, 7·1. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·3%) had m. p. 60·5—61° on crystallization from light petroleum–ether.

6-*Methoxy*-3-*methylindan*-1-*one.*—A mixture of the preceding acid (12·7 g.) and thionyl chloride (12 g.) was warmed to 45°. After 15 min. all the acid had dissolved and the reaction appeared to be complete in an hour. The excess of thionyl chloride was removed under reduced

[16] Lindenbaum, *Ber.*, 1917, **50**, 1373.

pressure at 100°, leaving the acid chloride as a pale yellow oil. To a stirred solution of this in carbon disulphide (30 ml.) at 0°, aluminium chloride (20·4 g.) was added during 30 min. and the whole was heated under reflux at 50° for 4 hr. After cooling, the mixture was shaken with ice, hydrochloric acid, and ether, and the organic phase separated and evaporated. The residue was redissolved in ether and washed with dilute aqueous sodium hydroxide and dried, and the solvent removed to give the indanone as a yellow oil (3·3 g., 29%).

5-*Methoxy*-1-*methylindane*.—The indanone (3·3 g.) was heated in acetic acid (100 ml.) for 55 hr. with zinc amalgam (14 g.) and hydrochloric acid (20 ml.). The solution was neutralised with aqueous sodium carbonate and extracted with ether which yielded a black oil (2·5 g.). When this was chromatographed on alumina, 1 : 3 benzene–light petroleum eluted the indane as a colourless oil (2·0 g., 65%).

1-*Methylindan*-5-*ol*.—The methoxy-methylindane (2·0 g.) was demethylated as described above in the preparation of 2-ethyl-3-methylphenol. 1-*Methylindan*-5-*ol* (1·4 g., 80%) was obtained as a brown solid which gave colourless prisms (0·5 g.), m. p. 55—55·5°, on recrystallizing from light petroleum (Found: C, 81·2; H, 8·1. $C_{10}H_{12}O$ requires C, 81·0; H, 8·2%); it gave a *phenylurethane*, m. p. 114° (Found: N, 5·1. $C_{17}H_{17}NO_2$ requires N, 5·2%).

6-*t*-*Butylindan*-5-*ol*.—Isobutene was passed through a molten mixture of indan-5-ol (67 g.) and toluene-*p*-sulphonic acid (3 g.) until the theoretical uptake had been achieved. The cooled mixture was dissolved in ether (200 ml.) and washed with 10% aqueous sodium hydroxide (100 ml.) and with water (50 ml.). Removal of the solvent yielded 6-*t*-*butylindan*-5-*ol* (70 g., 73%), m. p. 74° [from light petroleum (b. p. 40—60°)] (Found: C, 82·8; H, 9·6. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5%).

4-*Bromo*-6-*t*-*butylindan*-5-*ol*.—Bromine (32 g.; M/5) was added during 1 hr. to a stirred solution of 6-t-butylindan-5-ol (42 g., 0·22 mole) in acetic acid (125 ml.) at 10°, and stirring continued for a further 4 hr. After 48 hr. the mixture was poured into water (200 ml.) and extracted with ether, and the extract washed with aqueous sodium carbonate and water. Removal of the solvent gave 4-bromo-6-t-butylindan-5-ol as a brown oil (55 g., 95%).

4-*Bromoindan*-5-*ol*.—The crude butyl compound (55 g.) was heated with toluene-*p*-sulphonic acid (1 g.) for 3 hr. with a stream of carbon dioxide passing through the mixture. After cooling, the mixture was dissolved in ether, washed with 10% aqueous sodium carbonate solution (20 ml.), and extracted with 10% aqueous sodium hydroxide (150 ml.). A small amount (0·7 g.) of the alkali-insoluble butyl compound remained in the ether solution. The alkaline extract, on acidification followed by ether-extraction, gave a brown solid (38·7 g.) which yielded white needles of 4-bromoindan-5-ol (12·2 g.), m. p. 71—72° (lit.,[8] 73—74°).

4-*Bromo*-5-*methoxyindane*.—This compound, m. p. 66—67°, was prepared from the indanol by the method of Hunsberger *et al.*[8] who give m. p. 66°.

5-*Methoxy*-4-*methylindane*.—A solution of the bromo-compound (11·0 g.; 0·05 mole) in ether (50 ml.) was added to magnesium turnings (1·5 g.; 0·055 g.-atom) during 1 hr. and the whole refluxed for a further 3 hr. Dimethyl sulphate (12·6 g., 0·1 mole) in ether (20 ml.) was added and the mixture refluxed for 2 hr. Ice-cold 10% ammonium chloride solution (100 ml.) was added to the cooled mixture, and the ether layer was separated. From this a brown oil was recovered which on chromatography on deactivated alumina gave 5-methoxy-4-methylindane as a colourless oil (6·7 g., 83%; n_D^{25} 1·529).

4-*Methylindan*-5-*ol*.—The methoxy-methylindane (6·5 g.) was demethylated as described for the preparation of 2-ethyl-3-methylphenol. 4-*Methylindan*-5-*ol* (4·6 g., 77%) was obtained as needles, m. p. 98·5—99·5°, on twice recrystallizing from light petroleum (b. p. 40—60°) (Found: C, 81·1; H, 8·1. $C_{10}H_{12}O$ requires C, 81·0; H, 8·2%) [*phenylurethane*, m. p. 118° (Found: N, 5·3. $C_{17}H_{17}NO_2$ requires N, 5·2%)].

5-*Methoxy*-6-*methylindane*.—6-Bromo-5-methoxyindane (10·7 g.), m. p. 36°, prepared by the methylation of 6-bromo-5-indanol,[17] was dissolved in dry ether (30 ml.) and mixed with magnesium turnings (1·4 g.) during 1 hr. The mixture was then heated under reflux for 3 hr., then cooled, and dimethyl sulphate (11·8 g.) was added during 15 min. with stirring. The mixture was heated for 1½ hr. under reflux, left for 24 hr. and acidified with 2N-hydrochloric acid (50 ml.). It was then extracted with ether and washed with 10% sodium hydroxide solution and water, and the solvent removed, to give a brown oil (6·2 g.). This was chromatographed on silica gel to give crude 5-methoxy-6-methylindane as a colourless oil (3·8 g., 50%; n_D^{25} 1·545).

[17] Mills and Nixon, *J.*, 1930, 2510.

6-*Methylindan*-5-*ol*.—The above methoxy-methylindane (3·8 g.) was demethylated as described for 2-ethyl 3-methylphenol. The product was a pale yellow oil (2·9 g.) that was chromatographed on silica gel from which 1 : 9 benzene–light petroleum (b. p. 40—60°) eluted a white solid (0·97 g.). Recrystallization from light petroleum yielded needles of 6-methylindan-5-ol (0·44 g., 13%), m. p. 79—80·5° (Found: C, 81·1; H, 8·0. Calc. for $C_{10}H_{12}O$: C, 81·0; H, 8·2%). Fieser and Lothrop [7] give m. p. 83—84°. Further elution with 1 : 1 benzene–light petroleum gave a sticky solid (1·35 g.) which yielded indan-5-ol, m. p. and mixed m. p. 52—53°, on recrystallization from light petroleum.

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