118. *Synthesis of Cyclic Hydrocarbons. Part I.* o-*Dialkylbenzenes.*

By B. B. ELSNER, H. E. STRAUSS, and E. J. FORBES.

o-Diethyl-, *o*-ethylpropyl-, and *o*-ethyl*iso*propyl-benzene have been synthesised by unambiguous methods from readily available starting materials.

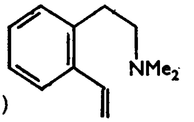
THE synthesis of pure hydrocarbons and the measurement of their physical constants, including spectrographic data, have in recent years become increasingly important for, *inter alia*, (*a*) analytical purposes, (*b*) the establishment of empirical relations between the physical properties and the structure of groups of compounds, and (*c*) the elucidation of the constitution of petroleum. In view of the paucity of reliable data, the synthesis of a series of *o*-dialkylbenzenes was undertaken. New synthetic methods have been investigated, which employ unambiguous routes.

Amongst the many hydrocarbons synthesised in this laboratory during the war was *o*-diethylbenzene.[1] Two preparations had been recorded previously; one,[2] using a Wurtz–Fittig reaction, gave a yield of less than 10%, and the second started from *o*-phenylenedipropionic acid, a compound which is not readily available. Birch *et al.*[3] later synthesised *o*-diethyl-, *o*-methylpropyl-, and *o*-methyl*iso*propyl-benzene in quantities of 1·5—2 l., by methods such that nearly all the intermediates used could be thoroughly purified. Other workers[4, 5, 6] used the Wurtz–Fittig reaction, or starting material obtained by separating mixtures of isomers, or methods leading only to symmetrical *o*-dialkylbenzenes.

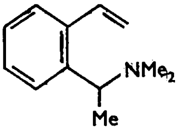
In this paper two methods for the preparation of *o*-diethylbenzene are described, one from *iso*quinoline (convenient for preparation of small quantities) and the second from phthalic anhydride, neither requiring fractional separation of positional isomers.

*iso*Quinoline was converted into 1 : 2 : 3 : 4-tetrahydro-1 : 2-dimethyl*iso*quinoline.[7] The methiodide of the latter could not be reduced with hydrogen and Adams catalyst in aqueous-alcoholic sodium acetate, though with the methiodide of 1 : 2 : 3 : 4-tetrahydro-2-methyl*iso*quinoline this reaction gives smoothly 2-methylphenethylamine as the sole product.[8] The failure here is probably due to steric hindrance, since models show that the *C*- and *N*-methyl groups together effect considerable shielding of the 1 : 2 carbon–nitrogen bond.

On Hofmann degradation 1 : 2 : 3 : 4-tetrahydro-1 : 2-dimethyl*iso*quinoline methiodide underwent ring fission smoothly and in good yield to give apparently a single substance, which probably has the structure (I), as in the reaction of the 1-benzyl analogue,[7] rather than the isomeric structure (II). On catalytic hydrogenation followed by Hofmann degradation the product gave *o*-ethylstyrene—this structure being independent of the nature (I) or (II) of the base—and immediate further hydrogenation gave *o*-diethylbenzene.



(I)



(II)

The second method, starting from phthalic anhydride, is outlined in the annexed scheme. Complete reduction of the carbonyl group of *o*-acetylbenzoic acid was

---

[1] E. J. Forbes, Thesis, Oxford, 1946.

[2] Voswinkel, *Ber.*, 1888, **21**, 3499; Bestian and Fries, *Ber.*, 1936, **69**, 715.

[3] Birch, Dean, Fidler, and Lowry, *J. Amer. Chem. Soc.*, 1949, **71**, 1362.

[4] Deluchat, *Ann. Chim.*, 1934, **1**, 181.

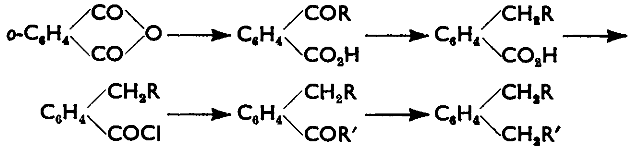
[5] Karabinos, Serijan, and Gibbons, *J. Amer. Chem. Soc.*, 1946, **68**, 2107.

[6] Nickels and Heintzelmann, *J. Org. Chem.*, 1950, **15**, 1142.

[7] Freud and Bode, *Ber.*, 1909, **42**, 1746.

[8] Emde and Kull, *Arch. Pharm.*, 1936, **274**, 183.

difficult.[9] The only successful method (which gave *o*-ethylbenzoic acid in 90% yield) was catalytic hydrogenation of aqueous sodium *o*-acetylbenzoate at 250°/120—150 atm. in presence of a copper–chromium oxide catalyst.[11] Temperature control was important: at 200—220° reduction was incomplete and at 280—290° a large proportion of resin was formed.



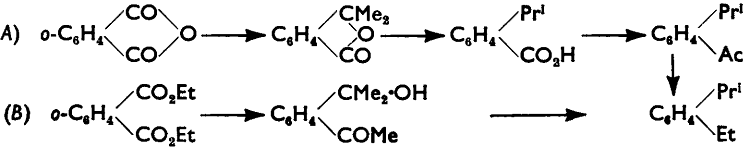
$$o\text{-}C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>O \longrightarrow C_6H_4\begin{matrix}COR\\CO_2H\end{matrix} \longrightarrow C_6H_4\begin{matrix}CH_2R\\CO_2H\end{matrix} \longrightarrow$$
$$C_6H_4\begin{matrix}CH_2R\\COCl\end{matrix} \longrightarrow C_6H_4\begin{matrix}CH_2R\\COR'\end{matrix} \longrightarrow C_6H_4\begin{matrix}CH_2R\\CH_2R'\end{matrix}$$

o-Propylbenzoic acid was prepared similarly from *o*-propionylbenzoic acid.

By the interaction of *o*-ethylbenzoyl chloride with a large excess of dimethylcadmium in benzene,[12] *o*-ethylacetophenone was obtained in 70% yield; *o*-propylacetophenone was obtained in 49% yield by the same method. Hydrogenation of *o*-ethylacetophenone at 230° under high pressure, with copper–chromium oxide catalyst, afforded a hydrocarbon containing a small proportion of diethyl*cyclo*hexane. However, by Huang-Minlon's method [10] both *o*-ethyl- and *o*-propyl-acetophenone were so readily reduced that the reaction proceeded below the temperature indicated by that author. When the excess of hydrazine hydrate was distilled from the reaction mixture, most of the hydrocarbon also distilled. Yields of over 80% were obtained.

o-*Ethyl*iso*propylbenzene.*—*o-iso*Propylbenzoic acid, an intermediate in the synthesis of *o*-ethyl*iso*propylbenzene, was prepared from diethyl phthalate, treatment of an ice-cold ethereal solution of which with ethereal methylmagnesium chloride (2 mols.) gave 3 : 3-dimethylphthalide. This compound can also be obtained by the reaction of the Grignard reagent with phthalic anhydride.[13] 3 : 3-Dimethylphthalide is a stable lactone,[14] which is only partly hydrolysed when dissolved in sodium hydroxide solution at 50°. However, treatment of this solution with hydrogen at 250°/110 atm. in presence of copper–chromium oxide catalyst gives a 95% yield of *o-iso*propylbenzoic acid. This reaction and the reduction of *o*-acetyl- and *o*-propionyl-benzoic acid, mentioned above, suggest that this hydrogenation may be a convenient method for the complete reduction of phthalides or of keto-acids which form phthalides on partial reduction.

Since *o-iso*propylbenzoic acid can be prepared readily it could be used in a synthesis (*A*) of *o*-ethyl*iso*propylbenzene. However, the shorter method (*B*) was employed. 2-*o*-Acetylphenylpropan-2-ol was prepared by the action of methylmagnesium chloride on diethyl phthalate in ether.[15] It is probable that the formation of a keto-alcohol rather than the diol in this reaction is due to a steric effect, since at a higher temperature, obtained by replacing the ether by benzene, the reaction proceeds further giving the diol.[15] Dehydration of the keto-alcohol yields a styrene in which the carbonyl group is in conjugation with the rest of the unsaturated system. It is therefore not surprising that the product obtained by dehydration with anhydrous copper sulphate polymerised to a soft rubber within 30 min. Huang-Minlon reduction of the keto-alcohol yielded a mixture of the



$$(A)\ o\text{-}C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>O \longrightarrow C_6H_4\left<\begin{matrix}CMe_2\\CO\end{matrix}\right>O \longrightarrow C_6H_4\begin{matrix}Pr^i\\CO_2H\end{matrix} \longrightarrow C_6H_4\begin{matrix}Pr^i\\Ac\end{matrix}$$
$$(B)\ o\text{-}C_6H_4\begin{matrix}CO_2Et\\CO_2Et\end{matrix} \longrightarrow C_6H_4\begin{matrix}CMe_2\cdot OH\\COMe\end{matrix} \longrightarrow C_6H_4\begin{matrix}Pr^i\\Et\end{matrix}$$

---

[9] Giebe, *Ber.*, 1896, **29**, 2533.
[10] Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.
[11] Adkins, Burgoyne, and Schneider, *ibid.*, 1950, **72**, 2626.
[12] Gilman and Nelson, *Rec. Trav. chim.*, 1936, **55**, 518; Cason, *Chem. Rev.*, 1947, **40**, 15.
[13] Bauer, *Ber.*, 1904, **37**, 735.
[14] Vène, Proc. XIth Intern. Congr. Pure Appl. Chem., London, 1947, **2**, 333.
[15] Bennett and Wain, *J.*, 1936, 1114.

original alcohol and an unsaturated compound. Therefore the keto-alcohol was hydrogenated under high pressure and at high temperature, with copper-chromium oxide catalyst. The yield of *o*-ethyl*iso*propylbenzene was only 27%, based on the keto-alcohol used.

o-*Di*iso*propylbenzene.*—1 : 2-Di-(1-hydroxy-1-methylethyl)benzene was prepared by Bennett and Wain's method.[15] Dehydration proceeded only to tetramethylphthalan. This was reduced with red phosphorus and hydriodic acid, but long heating was necessary before the hydrocarbon gave a satisfactory analysis and it seemed doubtful whether a really pure product could be obtained by this method.

Hydrogenation of the diol under high pressure, at 200°, in the presence of copper-chromium oxide, gave a mixture which contained some of the required hydrocarbon. The optimum conditions for the complete hydrogenation were not established.

The purity of the hydrocarbons, determined by means of a vapour-phase chromatogram, was in each case greater than 99%.

Further physical properties and the spectra will be published elsewhere.

EXPERIMENTAL

o-*Diethylbenzene. Method I.*—1 : 2-*Dihydro*-1 : 2-*dimethyl*iso*quinoline.*[7] *iso*Quinoline methiodide (54 g.) was added slowly to ethereal methylmagnesium iodide (from 10 g. of magnesium) at 0°. After 1 hr. the mixture was treated with ice and ammonium chloride, and the base (25·2 g., 79%) was isolated in the usual manner as a colourless oil, b. p. 123—124°/10 mm.

1 : 2 : 3 : 4-*Tetrahydro*-1 : 2-*dimethyl*iso*quinoline.* A solution of 1 : 2-dihydro-1 : 2-dimethyl-*iso*quinoline (13·9 g.) in ethanol (25 c.c.) was completely hydrogenated at 3 atm. with Adams catalyst (0·2 g.) in 30 min. and, after the catalyst had been removed, the mixture was distilled, giving the tetrahydro-base (90%) as a colourless oil, b. p. 110°/9 mm., n_D^{20} 1·5390. The *methiodide* (89%) crystallised in short needles (from ethanol), m. p. 186° (Found : C, 47·4; H, 5·8; N, 4·4; I, 42·1. $C_{12}H_{18}NI$ requires C, 47·5; H, 5·9; N, 4·7; I, 41·9%).

x-(o-*Ethylphenyl*)*ethyltrimethylammonium iodide* (x = 1 *or* 2). A solution of 1 : 2 : 3 : 4-tetrahydro-1 : 2-dimethyl*iso*quinoline methiodide (20 g.) in water (100 c.c.) was shaken with silver oxide (20 g.) at 60° for 1 hr. The solid was then filtered off, and the solution was evaporated *in vacuo* at $\not>$60° (higher temperatures resulted in decomposition and frothing). The residue was distilled under reduced pressure (bath-temp. 80°), and the amine was separated and distilled, to yield a colourless oil, b. p. 110°/15 mm. This was immediately dissolved in ethanol (15 c.c.) and hydrogenated under atmospheric pressure with Adams catalyst (0·1 g.). When reduction was complete (*ca.* 4 hr.) the catalyst was removed, the solvent was replaced by ether, and methyl iodide (8 c.c.) was added. After 2 hr. the precipitate was collected and twice recrystallised from ethyl acetate–light petroleum, affording x-(o-*ethylphenyl*)*ethyltrimethylammonium iodide* (9 g.) as plates, m. p. 173° (Found : C, 48·9; H, 6·6; N, 4·7; I, 40·1. $C_{13}H_{22}NI$ requires C, 48·9; H, 6·9; N, 4·4; I, 39·8%).

In one experiment methyl iodide was added to the amine obtained from the Hofmann degradation. The precipitate gave *trimethyl*-x-(o-*vinylphenyl*)*ethylammonium iodide* as rhombs, m. p. 138—139°, after two crystallisations from ethyl acetate–ethanol (Found : C, 49·0; H, 6·2; I, 39·9. $C_{13}H_{20}NI$ requires C, 49·2; H, 6·3; I, 40·1%).

o-*Diethylbenzene.* A solution of *x*-(*o*-ethylphenyl)ethyltrimethylammonium iodide (9·6 g.) in water (50 c.c.) was shaken with silver oxide (10·0 g.) at 60° for 45 min. The solid was separated, the solution evaporated *in vacuo*, and the residue distilled under reduced pressure (bath-temp. 130°), giving *o*-ethylstyrene. This was separated from some water, and hydrogenated in ethanol (10 c.c.) under atmospheric pressure with Adams catalyst (0·1 g.). When reduction was complete (*ca.* 1 hr.) the catalyst was removed, and the filtrate was distilled, giving *o*-diethylbenzene (Found : C, 89·3; H, 10·3. Calc. for $C_{10}H_{14}$: C, 89·6; H, 10·4%). The physical constants agreed with those of *o*-diethylbenzene prepared by method II.

o-*Diethylbenzene. Method II.*—o-*Acetylbenzoic acid.* This acid was prepared by the methods of de Benneville[16] and of Gabriel and Neumann.[17] The former method gave a 45% yield of the acid, based on phthalic anhydride, but the latter, although it gave a yield of only 25%, was more convenient for larger quantities. In this method the intermediate, phthalidylideneacetic acid, was best prepared in batches from 90 g. of phthalic anhydride, and

---

[16] de Benneville, *J. Org. Chem.*, 1941, **6**, 462.

[17] Gabriel and Neumann, *Ber.*, 1893, **26**, 952.

the products of several batches were combined for purification. Hydrolysis and decarboxylation of this acid yielded *o*-acetylbenzoic acid, which after recrystallisation first from benzene and then from water melted at 117—118°.

o-*Ethylbenzoic acid.* The keto-acid (15 g.) was neutralised (pH 8) with 15% sodium carbonate solution, and the salt was hydrogenated for 7 hr. at 250—255°/110 atm. (initial) in the presence of copper–chromium oxide (4 g.) (catalyst H.J.S.2).[11] After the autoclave had cooled, more catalyst (2 g.) was added, and the solution was treated under the same conditions for a further 7 hr. When cold the mixture was filtered, and acidified with concentrated hydrochloric acid; a pale yellow oil, which separated, crystallised in a few seconds. The acid (12·2 g., 89%) crystallised from water containing a small proportion of ethanol, and melted at 64—65° either alone or when mixed with a specimen obtained by Giebe's method.[9] Hydrogenation at 200° failed to reduce the keto-group completely, some 3-methylphthalide (b. p. 138—140°/12 mm.) being obtained when the solution was acidified. The acid was removed by dissolving the oily mixture in ether, and extracting this solution with sodium carbonate solution, thus leaving the lactone in the ethereal layer. Reduction at 280—290° and subsequent acidification also gave an oil; this slowly hardened to a white plastic mass. The product was distilled under reduced pressure, and yielded approx. 50% of *o*-ethylbenzoic acid, b. p. 139—140°/12 mm. The residue hardened to a brittle, clear, pale-brown resin. Attempted reduction of *o*-acetylbenzoic acid with hydrazine hydrate[10] yielded 1-hydroxy-4-methylphthalazine, m. p. 220° (Found: C, 67·7; H, 4·9; N, 17·1. Calc. for $C_9H_8ON_2$: C, 67·5; H, 5·0; N, 17·5%). With semicarbazide hydrochloride in pyridine, 2-*carbamyl*-3 : 4-*dihydro*-4-*methyl*-1-*oxophthalazine*, m. p. 224°, is formed (Found: C, 59·4; H, 4·5; N, 21·1. $C_{10}H_9O_2N_3$ requires C, 59·1; H, 4·5; N, 20·7%).

o-iso*Propylbenzoic acid.* A solution of methylmagnesium chloride (from magnesium, 9·6 g.) was added dropwise to a cold stirred solution of diethyl phthalate (44·4 g.) in ether (350 c.c.), and the suspension was stirred for 1 hr. at room temperature. 3 : 3-Dimethylphthalide (13·1 g.; b. p. 96—97°/0·1 mm.) crystallised from ether as thick colourless plates, m. p. 71° (Bauer[13] records m. p. 68°).

The phthalide (7·8 g.) dissolved completely in a small excess of warm sodium hydroxide solution (2·1 g. of sodium hydroxide in 5 c.c. of water). The cold solution was then diluted with water (35 c.c.), treated with hydrogen at 250—255°/110 atm. (initial) for 7 hr. in the presence of copper–chromium oxide (2 g.), filtered, and acidified with concentrated hydrochloric acid, whereupon white crystals of *o-iso*propylbenzoic acid (7·5 g., 95%; b. p. 160—161°/25 mm., m. p. 64°; anilide, m. p. 137°) were obtained (Found: C, 73·2; H, 7·3. Calc. for $C_{10}H_{12}O_2$: C, 73·2; H, 7·4%). Harvey[18] records m. p. 63—63·5° (anilide, m. p. 137—138°).

o-*Ethylacetophenone.* Anhydrous cadmium chloride (202 g.) was added to ethereal methylmagnesium chloride (from magnesium, 48 g.). The mixture was heated under reflux for 30 min.; the ether was then distilled and replaced progressively with dry benzene until the solvent distilled at 78°. *o*-Ethylbenzoyl chloride (88 g.; b. p. 97—98°/15 mm.) was added with stirring during 30 min. to this solution of dimethylcadmium cooled in ice–salt. The mixture was heated under reflux for 2 hr., then treated with ice and dilute sulphuric acid. *o*-Ethylacetophenone (55 g., 71%) was obtained as a colourless oil, b. p. 115—116°/30 mm., n_D^{18} 1·5250. The semicarbazone melted at 185°; Winkler[19] records m. p. 180°.

o-*Diethylbenzene.* Sodium (25 g.) was dissolved in diethylene glycol (440 c.c.), and *o*-ethylacetophenone (25 g.) was added, followed by 100% hydrazine hydrate (45 c.c.). The mixture was heated under reflux for 2 hr., then distilled until the temperature of the liquid reached 220°. The distillate contained most of the *o*-diethylbenzene. The residue was heated under reflux for 3 hr. When cold the solution was acidified and extracted with ether. The extract, combined with the distillate, was treated in the usual manner. After evaporation of the solvent, the residue was heated under reflux for 2 hr. over sodium; it was distilled, to give *o*-diethylbenzene (84%), b. p. 182·5—183°. The hydrocarbon was heated under reflux with potassium for 2 hr., and fractionally distilled through a Dixon column,[20] yielding a product with b. p. 182·9°/755 mm., n_D^{20} 1·5033, d_4^{20} 0·8796 (Birch *et al.*[3] record b. p. 183·3°/760 mm., n_D^{20} 1·5034).

Reduction of *o*-ethylacetophenone with hydrogen at 230°/110 atm. (initial) for 12 hr., with

[18] Harvey, *Acta Chem. Scand.*, 1954, **8**, 692.
[19] Winkler, *Chem. Ber.*, 1948, **81**, 256.
[20] Dixon, *J. Soc. Chem. Ind.*, 1949, **68**, 299.

copper–chromium oxide, gave a product whose boiling range, refractive index, and analysis indicated that it was chiefly *o*-diethylbenzene with a small amount of 1 : 2-diethyl*cyclo*hexane.

o-*Ethylpropylbenzene*.—o-*Propionylbenzoic acid*. *o*-Propylbenzoic acid (m. p. 93—94°), prepared by de Benneville's method,[16] was hydrogenated as described for the preparation of *o*-ethylbenzoic acid. The crude product, a pasty solid, was dissolved in ether, and the solution was extracted with sodium carbonate solution. The aqueous solution was heated to expel dissolved ether and, when cold, was acidified. *o*-Propylbenzoic acid separated as an oil (78%), which crystallised and had m. p. 58°, b. p. 164—165°/20 mm. Gottlieb[21] records m. p. 58°, b. p. 272°/739 mm.

o-*Propylacetophenone*. *o*-Propylbenzoyl chloride (80 g.; b. p. 111—112°/12 mm.) was allowed to react with dimethylcadmium, as described above, to give pale yellow o-*propylacetophenone* (39 g., 49%), b. p. 58—60°/0·04 mm., n_D^{16} 1·5203 (Found: C, 81·4; H, 8·9. $C_{11}H_{14}O$ requires C, 81·4; H, 8·7%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethanol as yellow needles, m. p. 131° (Found: C, 59·8; H, 5·5. $C_{17}H_{18}O_4N_4$ requires C, 59·6; H, 5·3%).

o-*Ethylpropylbenzene*. Reduction of *o*-propylacetophenone by Huang-Minlon's method[10] gave o-*ethylpropylbenzene* (83%), which when purified by distillation from potassium, followed by fractional distillation, had b. p. 200·9°/760 mm., n_D^{20} 1·4990, d_4^{20} 0·8732 (Found: C, 89·3; H, 10·8. $C_{11}H_{16}$ requires C, 89·1; H, 10·9%).

o-*Ethyl*iso*propylbenzene*.—2-*o*-Acetylphenylpropan-2-ol (m. p. 115°) was prepared by Bennett and Wain's method.[15] The 2 : 4-*dinitrophenylhydrazone* melted at 172° (Found: C, 57·3; H, 5·3; N, 15·4. $C_{17}H_{18}O_5N_4$ requires C, 57·0; H, 5·1; N, 15·6%). The alcohol was hydrogenated at 200—210°/115 atm. (initial) for 7 hr. with copper–chromium oxide (H.J.S.2).[11] The product was isolated in the usual manner, and distilled under reduced pressure. The middle fraction was heated under reflux with potassium for 1 hr., and twice fractionally distilled, yielding o-*ethyl*iso*propylbenzene*, b. p. 192·2°/752 mm., n_D^{20} 1·4980, d_4^{20} 0·8747 (Found: C, 88·9; H, 10·7. $C_{11}H_{16}$ requires C, 89·1; H, 10·9%). An attempt to reduce the keto-alcohol by Huang-Minlon's method gave an oil containing unchanged alcohol, which crystallised, and an unsaturated compound formed by the dehydration of the tertiary alcohol. An attempt to dehydrate the alcohol with anhydrous copper sulphate gave a viscous oil (b. p. 115—127°), which set to a transparent greenish gum within 0·5 hr.

o-*Di*iso*propylbenzene*.—*o*-Di-(1-hydroxy-1-methylethyl)benzene[15] (14·9 g.; m. p. 165—166°) was warmed with red phosphorus (6·2 g.) and acetic anhydride (88 c.c.) until all the crystals were dissolved. To the cooled solution 55% aqueous hydriodic acid (44 c.c.) was added dropwise and the mixture was heated under reflux for 2 hr. A further quantity of hydriodic acid (44 c.c.) was added, and the mixture was heated for 12 hr. When cold the mixture was diluted with water (500 c.c.), and sulphur dioxide was passed in until the colour was discharged. The oily layer was separated, washed, dried, and distilled from sodium. The hydrocarbon (7 g.; b. p. 202—203°), which probably contained some tetramethylphthalan, was again treated with red phosphorus and hydriodic acid as before. *o*-Di*iso*propylbenzene (5·1 g., 41%), b. p. 203—204°, n_D^{20} 1·4949, was obtained (Found: C, 89·1; H, 11·3. Calc. for $C_{12}H_{18}$: C, 88·8; H, 11·2%). Melpolder *et al.*[22] record b. p. 203·75°/760 mm., n_D^{20} 1·4960. It is uncertain whether all traces of impurity were removed from the product, and therefore the specimen could not be considered satisfactory for the determination of physical data.

Catalytic reduction of *o*-di-(1-hydroxy-1-methylethyl)benzene with hydrogen at 200°/115 atm. for 7 hr., in the presence of copper–chromium oxide, gave a product which distilled over a wide range. Only a small fraction boiled above 200°, and gave an analysis which was correct for *o*-di*iso*propylbenzene.

The absorption spectra and the purity of the *o*-dialkylbenzenes described in this paper are discussed in Part II.

The authors thank Sir Robert Robinson, O.M., F.R.S., for his interest and Dr. J. C. Smith for his advice and criticism.

THE DYSON PERRINS LABORATORY, OXFORD. [*Received, May 11th*, 1956.]

---

[21] Gottlieb, *Ber.*, 1899, **32**, 961.

[22] Melpolder, Woodbridge, and Headington, *J. Amer. Chem. Soc.*, 1948, **70**, 935.