

**741. The Preparation of the Five 2-Methyl-*x*-phenylpentanes.**

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The five 2-methyl-*x*-phenylpentanes have been prepared, all but 4-methyl-1-phenylpentane by new routes. Reduction of 2-methyl-1-phenylpent-1-en-3-one gave 2-methyl-1-phenylpentane, and of 4-methyl-4-phenylpentan-2-one gave 2-methyl-2-phenylpentane. 2-Methyl-3- and -4-phenylpentane have been obtained by use of phosphorylenes (Wittig-Schöllkopf reaction). 2-Methyl-4-phenylpentane has been synthesised by hydrogenolysis of 4-methyl-2-phenylpentan-2-ol.

THE five 2-methyl-*x*-phenylpentanes were required as reference compounds in a study of the alkylation of benzene by the 2-methylpent-*x*-enes, and as models for the unambiguous synthesis of more complex alkylbenzenes. Hence a number of alternative synthetic methods have been examined, and gas-liquid chromatography has been employed to establish purity and identity. Methods involving alkylation were avoided.

2-Methyl-1-phenylpentane has been prepared previously by (a) reduction of the unsaturated alcohol obtained from phenylmagnesium bromide and 2-methylpent-2-enal,<sup>1</sup> and (b) by two-stage reduction of  $\alpha$ -methylvalerophenone.<sup>2</sup> It also arises as a minor product in the sodamide cleavage of  $\alpha$ -benzyl- $\alpha$ -methylvalerophenone.<sup>3</sup> The hydrocarbon has now been obtained by a simple two-stage reduction of 2-methyl-1-phenylpent-1-en-3-one (1-benzylidenediethyl ketone); this is readily available by an acid-catalysed condensation; dilute aqueous alkali as catalyst yields the corresponding  $\beta$ -hydroxy-ketone in low yield.

Reported syntheses of 2-methyl-2-phenylpentane are (a) by alkylation of benzene by 2-chloro-2-methylpentane,<sup>4</sup> (b) by reduction of the product from alkylation of benzene with 4-chloro-4-methylpent-1-ene,<sup>5</sup> and (c) by reaction of the Grignard reagent from 2-methyl-2-phenylpropyl chloride with ethyl toluene-*p*-sulphonate.<sup>6</sup> Repetition of method (c) gave a 14% yield of the alkylbenzene but the latter is much more readily available by Wolff-Kishner reduction of 4-methyl-4-phenylpentan-2-one (from mesityl oxide and benzene).

2-Methyl-3- and 2-methyl-4-phenylpentane can be obtained by the same methods, the most frequently employed being that generally attributed to Klages.<sup>7</sup> This consists in dehydrating the appropriate tertiary alcohol and reducing the resultant olefin. In addition 2-methyl-3-phenylpentane has been prepared by sodamide cleavage of 2 : 2-dimethyl-1 : 3-diphenylpentan-1-one,<sup>8</sup> and the 4-isomer by dehydration of the tertiary alcohol obtained from phenylmagnesium and mesityl oxide, with subsequent reduction of the diene.<sup>9</sup> Klages's method has been repeated in both cases. The recent work of Wittig and Schöllkopf<sup>10</sup> has provided another method of generating hydrocarbons unambiguously, and this has been applied in this series. Ethylenetriphenylphosphine on reaction with *isobutyrophenone* gave a 1 : 1 mixture of *cis*- and *trans*-4-methyl-3-phenylpent-2-ene in 90% yield, while a 58% yield of 4-methyl-2-phenylpent-1-ene was obtained from methylenetriphenylphosphine and *isovalerophenone*. Reduction of the olefins afforded the required alkylbenzenes. A further variant of Klages's method consists

<sup>1</sup> Bjeluoss, *Ber.*, 1912, **45**, 625.

<sup>2</sup> Stenzl and Fichter, *Helv. Chim. Acta*, 1937, **20**, 846.

<sup>3</sup> Dumesnil, *Ann. Chim. (France)*, 1917, **8**, 70.

<sup>4</sup> Schreiner, *J. prakt. Chem.*, 1910, **82**, 292.

<sup>5</sup> Cologne and Garnier, *Bull. Soc. chim. France*, 1948, **15**, 436.

<sup>6</sup> Pines, Huntsman, and Ipatieff, *J. Amer. Chem. Soc.*, 1953, **75**, 2311.

<sup>7</sup> Klages, *Ber.*, 1904, **37**, 1721, 2301; Huston, Guile, Bailey, Curtis, and Esterdahl, *J. Amer. Chem. Soc.*, 1945, **67**, 899; Huston and Kaye, *ibid.*, 1942, **64**, 1576.

<sup>8</sup> Albesco, *Ann. Chim. (France)*, 1922, **18**, 216.

<sup>9</sup> Levina, Tantsyreva, Fainzilberg, and Mezentsova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1951, 161; *Chem. Abs.*, 1951, **45**, 9456.

<sup>10</sup> Wittig and Schöllkopf, *Ber.*, 1954, **87**, 1318.

in cleavage by sodium and ethanol in liquid ammonia of the tertiary benzylic alcohols:<sup>11</sup> applied to 4-methyl-2-phenylpentan-2-ol it constituted the easiest synthesis of unlimited quantities of 2-methyl-4-phenylpentane. However, only partial reduction of 2-methyl-3-phenylpentan-3-ol was achieved, and it was not possible to separate the alcohol from the hydrocarbon by distillation over sodium. The use of lithium-ethanol in both ammonia and diethylamine again only effected partial reduction. Since steric factors are unlikely to account for the difference in the behaviour of the alcohols, no explanation or rationalisation is offered.

The last alkylbenzene, 4-methyl-1-phenylpentane, has been made previously by Wurtz-Fittig reactions<sup>12</sup> and by reduction of  $\gamma$ -methylvalerophenone.<sup>13</sup> The last method has been repeated.

In general reference has not been made to alkylations which have yielded these alkylbenzenes, even though the reported physical constants are often in good agreement with those recorded here. Reference is made only to other formal synthetic studies, despite poorer agreement. Attention is drawn to Francis's comments<sup>14</sup> on the limited value of constants as a guide to purity and identity in this field.

#### EXPERIMENTAL

Infrared absorptions were measured on a G.S.2 Grubb-Parsons spectrometer. Gas-liquid chromatograms were effected on Apiezon L supported on C-22 firebrick at 213°. M. p.s were taken on a Kofler block and are uncorrected.

*2-Methyl-1-phenylpent-1-en-3-one.*—Diethyl ketone (22.8 g.), benzaldehyde (28.0 g.), and 10N-hydrochloric acid (55 ml.) were heated under reflux for 4 hr. (cf. ref. 15). The cooled mixture was extracted with ether, and the combined extracts were washed with water, sodium hydrogen carbonate solution, and water. The dried (MgSO<sub>4</sub>) extract was evaporated, and the residue distilled to give the unsaturated ketone, b. p. 122—124°/5 mm. (lit.,<sup>16</sup> 163°/20 mm.), which crystallised (21.8 g., 53%);  $\nu_{\max}$ , 1661 (CO·C=C), 1623 (Ph·C=C), and 802 (CR<sub>2</sub>=CHR) cm.<sup>-1</sup>. The 2:4-dinitrophenylhydrazone, red prisms from ethanol-chloroform, had m. p. 181—183° (Found: C, 61.1; H, 4.7; N, 16.1. C<sub>18</sub>H<sub>18</sub>O<sub>4</sub>N<sub>4</sub> requires C, 60.9; H, 5.1; N, 15.8%). The semicarbazone, from benzene, had m. p. 183° (lit.,<sup>16</sup> 188°) (Found: C, 67.3; H, 7.5; N, 18.1. Calc. for C<sub>13</sub>H<sub>17</sub>ON<sub>3</sub>: C, 67.4; H, 7.3; N, 18.2%).

The same product was obtained in 9% overall yield by dehydrating (toluene-*p*-sulphonic acid) 1-hydroxy-2-methyl-1-phenylpentan-3-one, b. p. 131—137°/3 mm., which was formed by stirring together for 3 days benzaldehyde (42.0 g.), diethyl ketone (118.5 ml.), water (40 ml.), ethanol (95 ml.), and 10% sodium hydroxide solution (10 ml.).

*2-Methyl-1-phenylpentan-3-one.*—2-Methyl-1-phenylpent-1-en-3-one (18.2 g.) was hydrogenated in ethanol in the presence of 10% palladium-carbon until 1 mol. of hydrogen had been absorbed. The ketone had b. p. 244—251°,  $n_D^{20}$  1.5037 (15.5 g., 84%),  $\nu_{\max}$ , 1706 (sat. C=O), 742 (Ph), and 700 (Ph) cm.<sup>-1</sup> (Found: C, 81.5; H, 9.3. C<sub>12</sub>H<sub>16</sub>O requires C, 81.7; H, 9.1%). The 2:4-dinitrophenylhydrazone, yellow rhombs from ethanol-chloroform, had m. p. 159° (Found: C, 60.7; H, 5.7; N, 15.9. C<sub>18</sub>H<sub>20</sub>O<sub>4</sub>N<sub>4</sub> requires C, 60.7; H, 5.6; N, 15.7%). The semicarbazone, needles from benzene-light petroleum (b. p. 40—60°), had m. p. 116—117° (Found: C, 66.4; H, 7.9; N, 17.9. C<sub>13</sub>H<sub>19</sub>ON<sub>3</sub> requires C, 66.8; H, 8.1; N, 18.0%).

*2-Methyl-1-phenylpentane.*—2-Methyl-1-phenylpentan-3-one (11.5 g.), potassium hydroxide pellets (12.4 g.), and 80% hydrazine hydrate (8.8 ml.) yielded, by the Huang-Minlon modification<sup>17</sup> of the Wolff-Kishner reduction, the alkylbenzene, b. p. 210—218° (6.23 g., 59%). Redistillation over sodium gave an analytical specimen, b. p. 216—218°,  $n_D^{20}$  1.4880 (lit., 214°/740 mm.<sup>2</sup>;  $n_D^{25}$  1.4827<sup>1</sup>) (Found: C, 89.1; H, 11.0. Calc. for C<sub>12</sub>H<sub>18</sub>: C, 89.9; H, 11.1%).

*2-Methyl-2-phenylpentane.*—(a) 4-Methyl-4-phenylpentane-2-one, prepared in 86% yield from benzene and mesityl oxide, had b. p. 145°/37 mm. (lit.,<sup>18</sup> 134°/22 mm.),  $\nu_{\max}$ , 1704 (sat. C=O),

<sup>11</sup> Birch, *J.*, 1945, 809.

<sup>12</sup> Schramm, *Annalen*, 1883, **218**, 383; Stenzl and Fichter, *Helv. Chim. Acta*, 1934, **17**, 669.

<sup>13</sup> Berliner and Berliner, *J. Amer. Chem. Soc.*, 1950, **72**, 222.

<sup>14</sup> Francis, *Chem. Rev.*, 1948, **42**, 107.

<sup>15</sup> Metayer and Epinau, *Compt. rend.*, 1948, **226**, 1095.

<sup>16</sup> Vorlander, *Annalen*, 1896, **294**, 253.

<sup>17</sup> Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.

<sup>18</sup> Hoffman, *ibid.*, 1929, **51**, 2542.

1030 (vs), 763 (Ph), and 697 (Ph)  $\text{cm}^{-1}$ . Wolff-Kishner reduction as above gave, after re-distillation over sodium, the alkylbenzene (70%), b. p. 206—208°,  $n_D^{20}$  1.4935. Homogeneity and identity were established by comparison of the infrared spectrum with that of the specimen prepared as below, and by gas-liquid chromatography.

(b) Preparation of the alkylbenzene by the method of Pines *et al.*<sup>6</sup> from the Grignard reagent of 2-methyl-2-phenylpropyl chloride (b. p. 112—114°/21 mm.,  $n_D^{20}$  1.5232) and ethyl toluene-*p*-sulphonate gave the hydrocarbon (14% yield), b. p. (from sodium) 196—197°,  $n_D^{20}$  1.4943 (lit.,<sup>4-6</sup> 126.8—127°/66 mm., 205—206°;  $n_D^{20}$  1.4929). The infrared absorption was identical with the published curve,<sup>6</sup> and the product was shown to be homogeneous by gas-liquid chromatography.

2-Methyl-3-phenylpentan-3-ol.—*iso*Butyrophenone (b. p. 221—223°,  $n_D^{20}$  1.5175; 2:4-dinitrophenylhydrazone, m. p. 161—162°) with ethylmagnesium bromide gave the tertiary alcohol (95%), b. p. 107—109°/11 mm.,  $n_D^{20}$  1.5153 (lit.,<sup>19,7</sup> 125—130°/25 mm., 106—112°/8 mm.,  $n_D^{20}$  1.5155) (Found: C, 80.9; H, 10.3. Calc. or  $\text{C}_{12}\text{H}_{18}\text{O}$ : C, 81.0; H, 10.1%).

2-Methyl-3-phenylpentane.—The above alcohol on dehydration (toluene-*p*-sulphonic acid) yielded the calculated amount of water and gave the corresponding olefin(s) (55% yield), b. p. 201°,  $n_D^{20}$  1.5151 (lit.,<sup>19,20</sup> 206—208°,  $n_D^{20}$  1.5104,  $n_D^{18.7}$  1.5131),  $\nu_{\text{max}}$ . 1656 ( $\text{Ar}\cdot\text{C}=\text{C}$ ), 830 (w) ( $\text{CHR}=\text{CR}_2$ )  $\text{cm}^{-1}$ . Quantitative reduction in ethanol in the presence of platinum gave 2-methyl-3-phenylpentane, b. p. 213°,  $n_D^{20}$  1.4851 (lit.,<sup>6,9</sup> 199—200°, 207—209°,  $n_D^{20}$  1.4890, 1.4912) (Found: C, 88.6, H, 11.0%).

4-Methyl-3-phenylpent-2-ene.—Ethyltriphenylphosphonium bromide (23.2 g.; m. p. 205.5°) was added in small portions to a stirred 1.34N-ethereal solution of *n*-butyl-lithium (50 ml.) under nitrogen. Then the red solution was heated under reflux for 5 hr., and *isobutyrophenone* (11 ml.) in ether (50 ml.) added during 45 min. to the cooled solution. The mixture was next heated under reflux for 4 hr., cooled, and filtered. The residue was washed with ether, and the combined filtrates washed with water, dried ( $\text{MgSO}_4$ ), and evaporated. The residual yellow oil was chromatographed on alumina in light petroleum (b. p. 40—60°) to yield the olefins (8.92 g., 90%), b. p. 208—210°,  $n_D^{20}$  1.5080. Gas-liquid chromatography showed that the product was a 1:1 mixture of the *cis*- and *trans*-isomers (relative retention volume  $1.249 \pm 0.006$ ),  $\nu_{\text{max}}$ . 830 ( $\text{CHR}=\text{CR}_2$ )  $\text{cm}^{-1}$  (Found: C, 90.3; H, 10.0.  $\text{C}_{12}\text{H}_{16}$  requires C, 90.0; H, 10.0%). Reduction in the presence of platinum in ethanol gave a quantitative yield of 2-methyl-3-phenylpentane, whose homogeneity and identity were established by infrared absorption and gas-liquid chromatography.

Attempted Hydrogenolysis of 4-Methyl-3-phenylpentan-3-ol.—Under the conditions used successfully for 4-methyl-2-phenylpentan-2-ol (see below), only partial reduction, as shown by infrared absorption and gas-liquid chromatography, was obtained. Neither prolonging the reaction time nor the use of lithium-ethanol, in liquid ammonia or in diethylamine, materially increased the yield. Further it was not possible to separate the tertiary alcohol from the required hydrocarbon by distillation from sodium.

4-Methyl-2-phenylpentan-2-ol.—*iso*Butyl methyl ketone with phenylmagnesium bromide gave the tertiary alcohol (86% yield), b. p. 105—107°/11 mm.,  $n_D^{20}$  1.5072 (lit.,<sup>19,21</sup> 125—129°/14 mm.,  $n_D^{16}$  1.5157) (Found: C, 81.0; H, 10.2%).

2-Methyl-4-phenylpentane.—(a) Dehydration of the preceding alcohol in the usual manner yielded the calculated amount of water and gave the olefin(s), b. p. 203°,  $n_D^{20}$  1.5151 (lit.,<sup>8,21</sup> 207°, 216—220°,  $n_D^{10}$  1.5231,  $n_D^{15}$  1.516). Quantitative reduction in ethanol in the presence of platinum gave the required alkylbenzene, b. p. 205—206°,  $n_D^{20}$  1.4850. The homogeneity and identity of the product were established by comparison of the infrared spectrum and gas-liquid chromatographic behaviour with those of the hydrocarbon prepared as below.

(b) 4-Methyl-2-phenylpentan-2-ol (35.6 g.) was hydrogenolysed as described by Birch<sup>11</sup> to yield the hydrocarbon (59%), b. p. 205—206°,  $n_D^{20}$  1.4850 (lit.,<sup>7,9</sup> 197—198°/735 mm.,  $n_D^{20}$  1.4856, 1.4824) (Found: C, 88.5; H, 11.2%).

4-Methyl-2-phenylpent-1-ene.—Methyltriphenylphosphonium iodide (33.0 g.; m. p. 183°) was added in small portions to a stirred 0.52N-ethereal solution of *n*-butyl-lithium (150 ml.) under nitrogen during  $\frac{1}{2}$  hr. *iso*Valerophenone (15 ml.) was added to the red solution and the mixture stirred for 2 hr., then filtered. The residue was washed with ether, and the combined filtrates

<sup>19</sup> Protiva *et al.*, *Chem. Listy.*, 1952, **46**, 47; *Chem. Abs.*, 1952, **46**, 8004; Apolit, *Ann. Chim. (France)*, 1924, **2**, 71.

<sup>20</sup> Auwers and Eisenlohr, *J. prakt. Chem.*, 1910, **82**, 65.

<sup>21</sup> Bodroux and Taboury, *Bull. Soc. chim. France*, 1909, **5**, 812; *Compt. rend.*, 1909, **148**, 1675.

were washed with water, dried, and evaporated. The residue was chromatographed on alumina in light petroleum (b. p. 40—60°) to give the *olefin* (7.68 g., 58%), b. p. 209°,  $n_D^{20}$  1.5100,  $v_{\max}$ . 1799, 1625 (ArC=C), 985 (R<sub>2</sub>C=CH<sub>2</sub>), 776 (Ph) cm.<sup>-1</sup>. The olefin was shown to be homogeneous by gas-liquid chromatography (Found: C, 90.1; H, 10.0%). Reduction of the olefin in the presence of platinum yielded 2-methyl-4-phenylpentane quantitatively, identity and homogeneity being established by infrared absorption and gas-liquid chromatography.

*4-Methyl-1-phenylpentane*.—This was prepared in 70% yield by reduction of  $\gamma$ -methylvalerophenone (b. p. 136°/17 mm.) by the Wolff-Kishner method as in previous cases. It had b. p. 99—100°/16 mm.,  $n_D^{20}$  1.4860 (lit.,<sup>13</sup> 219°,  $n_D^{20}$  1.4853). The homogeneity of the hydrocarbon was confirmed by gas-liquid chromatography.

*Gas-Liquid Chromatography*.—The relative retention volumes of the five alkylbenzenes were: 2-methyl-3- and -4-methylpentane (irresolvable) 1.000; 2-methyl-2-phenylpentane 1.126  $\pm$  0.002; 4-methyl- 1.270  $\pm$  0.006 and 2-methyl-1-phenylpentane 1.222  $\pm$  0.003.

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