

(5) M. Gomberg and C. C. Buchler, *ibid.*, **42**, 2086 (1920).

radical into the known structures (VIII) and (IX), using the procedures previously studied for similar series involving the diphenylmethyl⁶ and triphenylmethyl group.⁷ Each of these products (VI) and (VII) were characterized by means of their α -naphthylurethan and *p*-nitrobenzyl ethers.

Experimental

Preparation of Benzyl *o*-Tolyl Ether (V).—A solution of 162 g. of *o*-cresol in 600 ml. of 1.5 *M* sodium hydroxide was treated with 126 g. of benzyl chloride and refluxed for one hour. Upon cooling, the mixture was extracted with ether, the ether extract washed with water, then with 10% potassium hydroxide to remove excess *o*-cresol and again with water. The ether extract was dried over anhydrous sodium sulfate and after removal of the solvent, the product was recovered by distillation at 144–145° and 3 mm. pressure yielding 77.8 g. (n_D^{25} 1.5730) of the desired ether.

Rearrangement of Benzyl *o*-Tolyl Ether (V).—Seventy grams (0.35 mole) of the ether was heated with 50 g. of zinc chloride for five hours at 160–170°. At the end of this time the mixture was poured into water and the resulting oil was extracted with ether, dried over anhydrous sodium sulfate, and after removal of the ether the total yield was fractionated through a Podbielniak type column at 30 mm. yielding the following fractions: (1) 5.4 g., b.p. to 98°, n_D^{25} 1.5411 corresponding to *o*-cresol, I whose dibromo derivative, m.p. 55°, agreed with a known sample. (2) 16.4 g., b.p. 202–208°, n_D^{25} 1.5860 corresponding to the ortho benzyl rearranged product, II. The α -naphthylurethan derivative melted at 139–140°. *Anal.* Calcd. for $C_{25}H_{21}O_2N$: C, 81.7; H, 5.8; N, 3.8. Found: C, 82.1; H, 5.88; N, 3.7. The oxyacetic acid derivative melted at 84–85°. *Anal.* Calcd. for $C_{16}H_{14}O_3$: C, 74.9; H, 6.3. Found: C, 73.9; H, 6.5. (3) 11.4 g., b.p. 212–216°, n_D^{25} 1.5911 corresponding to the para benzyl rearranged product, III. The α -naphthylurethan derivative melted at 143° (mixed m.p. with derivative of II, 125–132°). *Anal.* Calcd. for $C_{25}H_{21}O_2N$: C, 81.7; H, 5.8; N, 3.8. Found: C, 81.5; H, 5.9; N, 4.1. The oxyacetic acid derivative melted at 110–111°. *Anal.* Calcd. for $C_{16}H_{14}O_3$: C, 74.9; H, 6.3. Found: C, 74.3; H, 6.4. (4) 14.5 g., b.p. 290–295°, n_D^{25} 1.6102 corresponding to the dibenzyl product, IV. *Anal.* Calcd. for $C_{27}H_{26}O$: C, 87.5; H, 6.92. Found: C, 87.7; H, 6.88. The α -naphthylurethan derivative melted at 175°. *Anal.* Calcd. for $C_{32}H_{27}O_2N$: C, 83.9; H, 5.9; N, 3.0. Found: C, 83.8; H, 6.2; N, 3.2. The oxyacetic acid derivative melted at 126–127°. *Anal.* Calcd. for $C_{23}H_{22}O_3$: C, 79.8; H, 6.36. Found: C, 79.9; H, 6.14.

Benzylation of *o*-Cresol.—To a mixture of 100 g. of *o*-cresol and 100 g. of benzyl alcohol in 200 ml. of petroleum ether, 65 g. of anhydrous aluminum chloride was added over a half-hour period while the mixture was mechanically stirred and heated on a steam-bath. At the end of one hour the semi-solid mixture was poured into 300 ml. of ice-water to which 50 ml. of concentrated hydrochloric acid had been added. The oil which separated was extracted with ether and dried over anhydrous potassium carbonate. After removal of the ether, the residue was fractionally distilled at 5 mm. to produce six fractions: (1) 42.7 g., b.p. to 138°; (2) 43.1 g., b.p. 160–164°; (3) 15 g., b.p. 165–195°; (4) 11.7 g., b.p. 215–235°; (5) 18.6 g., b.p. 235–240°; (6) 5.7 g., b.p. 240–265°. This indicated a mixture of the mono-benzyl derivatives in fraction 1 and 2 and the dibenzyl product principally in fraction 5 (4a). For more complete identification, fractions 1 and 2 were combined and fraction-

ated in the Podbielniak type column at 35 mm. pressure yielding 20 g., b.p. 202–204°, n_D^{25} 1.5870 corresponding to II and 44.4 g., b.p. 211–214°, n_D^{25} 1.5937 corresponding to III. These fractions solidified and were characterized and comparisons made to prove the similarity of products to those produced by direct rearrangement.

Preparation and Characterization of 4-Bromo-6-benzyl-*o*-cresol (VI).—Four grams of 6-benzyl-*o*-cresol (II) was brominated in 50 ml. of glacial acetic acid with 3.2 g. of bromine in the presence of iron tacks. Fumes of hydrogen bromide appeared and after two hours the reaction mixture was poured onto ice and the resultant oil solidified. The product was recrystallized from ligroin and melted at 62.5–63.5°.

The same product was prepared when 63 g. of 4-bromo-*o*-cresol (VIII),⁷ dissolved in 200 g. of concentrated sulfuric acid and 200 g. of glacial acetic acid, was treated with 18 g. of benzyl alcohol dissolved in 50 g. of glacial acetic acid. Oil started to separate and after 24 hours the oily layer was separated and combined with further oil thrown out by pouring the acid layer onto ice. Fractionation of the oil at 100–106° and 1 mm. pressure gave 16.5 g. of unchanged 4-bromo-*o*-cresol and at 165–171° and 1 mm. pressure gave 13.5 g. of benzylated product. After recrystallization from ligroin it melted at 63°.

In a second method of condensation, 45 g. of 4-bromo-*o*-cresol (VIII) and 25 g. of benzyl alcohol, dissolved in 60 ml. of petroleum ether, was treated with 25 g. of anhydrous aluminum chloride during a one-half hour period. After standing overnight the reaction product was poured onto a mixture of ice and 30 ml. of concentrated hydrochloric acid. The resulting oil was extracted with ether, dried and fractionally distilled at 6 mm. pressure producing 26 g. of unchanged 4-bromo-*o*-cresol and 6 g. of product collected between 180–190°. Each of the condensed products gave no depression in m.p. when mixed with the product of direct bromination above.

Preparation and Characterization of 6-Bromo-4-benzyl-*o*-cresol (VII).—Five grams of 4-benzyl-*o*-cresol (III) was brominated in carbon tetrachloride solution with 4 g. of bromine. Fumes of hydrogen bromide appeared and after three hours the solvent was removed by evaporation and the reddish-brown oil fractionally distilled at 6 mm. pressure and at 183–185°, giving a yield of 3 g. or 30%.

The same product was prepared when 63 g. of 6-bromo-*o*-cresol (IX),⁷ dissolved in 200 g. of concentrated sulfuric acid and 200 g. of glacial acetic acid, was treated with 18 g. of benzyl alcohol dissolved in 50 g. of glacial acetic acid. Oil started to separate and after 24 hours the oily layer was separated and combined with further oil thrown out by pouring onto ice. By fractionation, 25 g. of unchanged 6-bromo-*o*-cresol was recovered and at 165–169° and 1 mm. pressure 20 g. of benzylated product was collected.

A second method of condensation employed 45 g. of 6-bromo-*o*-cresol (IX) and 25 g. of benzyl alcohol dissolved in 60 ml. of petroleum ether, to which 25 g. of aluminum chloride was added during the course of 30 minutes. After standing overnight the mixture was added to ice and hydrochloric acid and the resulting oil was taken up in ether. Upon distillation 8 g. of a light straw-colored oil came over between 179–181° at 5 mm. pressure and as in the previous instances did not crystallize.

The α -naphthylurethan derivative of VI melted at 154–156°. *Anal.* Calcd. for $C_{25}H_{23}O_2NBr$: C, 67.2; H, 4.5. Found: C, 68.3; H, 4.8. The α -naphthylurethan of VII melted at 152–153° (mixed melting points of derivatives of VI and VII, 136–141°). *Anal.* Calcd. for $C_{25}H_{23}O_2NBr$: C, 67.2; H, 4.5. Found: C, 67.4; H, 4.8. The *p*-nitrobenzyl ether of VI melted at 110–111°. *Anal.* Calcd. for $C_{24}H_{18}O_3NBr$: Br, 19.38. Found: Br, 19.0. The *p*-nitrobenzyl ether of VII melted at 81.5–82.5°. *Anal.* Calcd. for $C_{24}H_{18}O_3NBr$: Br, 19.38. Found: Br, 19.5.

(6) H. A. Iddles, D. C. Chadwick, J. W. Clapp and R. T. Hart, *THIS JOURNAL*, **64**, 2154 (1942).

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