

*Anal.* Calcd. for  $C_7H_6OBr_2$ : Br, 60.15. Found: Br, 60.01.

The less soluble phenol formed with it is therefore the 2,4-dibromo-3-methylphenol.

**Preparation of 4,6-Dibromo-3-methylphenol from 3-Amino-4,6-dibromotoluene.**—Pure *m*-toluidine was acylated and treated in cold acetic acid solution with two molecular equivalents of bromine. The acyl group was removed by means of alcoholic potash, and the 4,6-dibromo-*m*-toluidine was recrystallized from alcohol to a constant melting point of 75–76°. The purified amine was dissolved in hot, dilute hydrochloric acid, filtered and cooled to 0°. The calculated quantity of sodium nitrite was slowly added and the mixture was stirred until solution was complete. After two hours the diazonium salt was decomposed by heating on the water-bath and the dark colored mixture was steam distilled. The distillate was salted out and extracted with ether. After evaporation of the solvent the phenol was separated from the quinone by dissolving in dilute sodium hydroxide, reprecipitating with hydrochloric acid, and extracting with ether. The purified 4,6-dibromo-3-methylphenol crystallized from petroleum ether in fine flat crystals which cling to the sides of the beaker. The melting point (65–66°) is ten degrees higher than that given by Gibbs and Robertson.<sup>7</sup> The benzoyl derivative came down from alcohol in fine needles melting at 84–85°.

*Anal.* Calcd. for  $C_{14}H_{10}O_2Br_2$ : Br, 43.2. Found: Br, 43.78.

### Summary

Bromination of *m*-cresol in the cold with one molecular equivalent of bromine gave a mixture of 4-bromo-3-methylphenol and 6-bromo-3-methylphenol.

Bromination of *m*-cresol with two molecular equivalents of bromine gave a mixture of 2,4-dibromo-3-methylphenol and 4,6-dibromo-3-methylphenol.

<sup>9</sup> Neville and Winther, *Ber.*, **13**, 971 (1880).

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## ACTION OF AROMATIC ALCOHOLS ON AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE. VIII. BENZYLATION OF META-CRESOL

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This completes a series of three articles from this Laboratory on the benzylation of the cresols.<sup>1</sup>

*m*-Cresol treated with benzyl alcohol and aluminum chloride in petroleum ether gave two monobenzyl cresols and one dibenzyl cresol: 3-methyl-4-benzylphenol,<sup>2</sup> 3-methyl-6-benzylphenol and 3-methyl-4,6-dibenzylphenol. When treated with sodium and benzyl chloride in toluene (Claisen reaction)<sup>3</sup> it gave also two monobenzyl cresols and one dibenzyl cresol: 3-methyl-2-benzylphenol, 3-methyl-6-benzylphenol and 3-methyl-2,6-dibenzyl-

<sup>1</sup> Huston and others, *THIS JOURNAL*, **52**, 4484 (1930); **53**, 2379 (1931).

<sup>2</sup> Venturi, *Gazz. chim. ital.*, **31**, I, 472 (1901).

<sup>3</sup> Claisen, *Ann.*, **442**, 221 (1924).

phenol, and a trace of the dibenzyl derivative obtained in the aluminum chloride condensation. This is interesting in that it represents a small amount of para substitution by the Claisen reaction. Both types of condensation yielded 3-methyl-6-benzylphenol as the only common product. In the Claisen condensation a small amount of the ether, 3-methylphenyl benzyl ether, was isolated.

The 3-methyl-2,6-dibenzylphenol was also prepared from 3-methyl-2-benzylphenol and benzyl chloride by the Claisen reaction. This condensation gave a small amount of the ether, 2-benzyl-3-methylphenyl benzyl ether.

Benzoyl derivatives of all the benzylated cresols were prepared, and bromine derivatives of all except 3-methyl-2,6-dibenzylphenol, this bromine derivative being, like the benzylated cresol itself, a liquid and obtained in our work in insufficient quantity to purify.

In order to establish the structures assigned to the various benzylated cresols, two dibromo-*m*-cresols were benzylated by the Claisen method. In 2,4-dibromo-*m*-cresol<sup>4</sup> only the 6-position is available for the benzyl group to enter. The product obtained, 2,4-dibromo-3-methyl-6-benzylphenol, was identical with that obtained by brominating 3-methyl-6-benzylphenol. The 2,4-dibromo-*m*-cresol used was prepared by direct bromination of *m*-cresol and melted at 64–65°.

The benzylation of 4,6-dibromo-*m*-cresol,<sup>4</sup> prepared from 4,6-dibromo-*m*-toluidine by diazotization to the phenol (m. p. 65–66°), gave the other *o*-benzyl derivative, 4,6-dibromo-3-methyl-2-benzylphenol, the same compound that was prepared by brominating 3-methyl-2-benzylphenol.

It is worthy of note that the aluminum chloride method did not introduce a benzyl group between the phenolic hydroxyl and the methyl group of *m*-cresol; also that of the two monobenzyl derivatives in which the benzyl groups are ortho to the phenolic hydroxyl, the one which is the more compact and symmetrical has the higher melting point.<sup>5</sup>

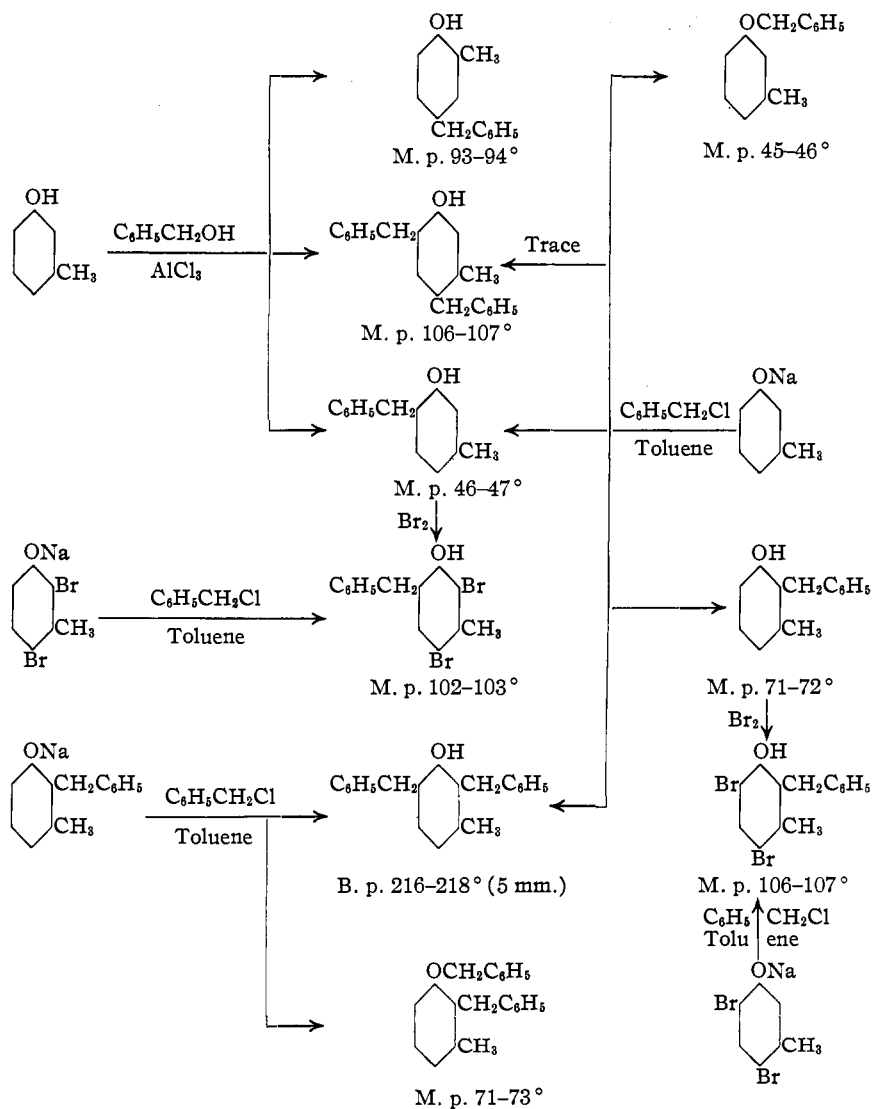
### Experimental

**Benylation of *m*-Cresol by the Aluminum Chloride Method.**—A mixture of 120 g. of *m*-cresol, 100 g. of benzyl alcohol, and 150 g. of petroleum ether was placed in a tall vessel and stirred constantly during the addition of 60 g. of aluminum chloride over a period of about two hours. The temperature was maintained at about 35° and additional petroleum ether was added occasionally. Hydrogen chloride was given off copiously and the substance became a light brown viscous mixture. After standing overnight it was decomposed with ice, extracted with ether and distilled. The following fractions were obtained at 4 mm.: 125–140°, 6.0 g.; 140–165°, 38.0 g.; 165–185°, 33.0 g.; 185–250°, 46.5 g.

**3-Methyl-6-benzylphenol.**—The fraction 140–165° boiled mostly at 153–157°. It was a thick yellow oil which solidified after standing for some time in the refrigerator. Crystallization had to be carried out in a cold place. The substance came out in a mass

<sup>4</sup> Huston and Hutchinson, *THIS JOURNAL*, **54**, 1504 (1932).

<sup>5</sup> Carnelley, *Phil. Mag.*, [5] **13**, 116 (1882).



of white, felted, needle-like crystals melting at 46–47° and boiling at 153–155° (4 mm.). This was also prepared by the Claisen method.

*Anal.* Subs., 0.2797, 0.3157: CO<sub>2</sub>, 0.8638, 0.9719; H<sub>2</sub>O, 0.1792, 0.2004. Calcd. for C<sub>14</sub>H<sub>14</sub>O: C, 84.8; H, 7.12. Found: C, 84.23, 83.96; H, 7.17, 7.10.

**3-Methyl-4-benzylphenol.**—The fraction 165–185° solidified in the receiver and was crystallized from petroleum ether in colorless prisms melting at 93–94° and boiling at 168–170° (5 mm.).

*Anal.* Subs., 0.2154: CO<sub>2</sub>, 0.6680; H<sub>2</sub>O, 0.1381. Calcd. for C<sub>14</sub>H<sub>14</sub>O: C, 84.8; H, 7.12. Found: C, 84.57; H, 7.17.

**3-Methyl-4,6-dibenzylphenol.**—The fraction 185–250° nearly all came over at 220–230° and solidified to form an oily mass which, after several crystallizations, came out as a very soft, felted, white mass, melting at 106–107° and boiling at 230–232° (5 mm.).

The assignment of structure was based upon the non-formation of 3-methyl-2-benzylphenol by the aluminum chloride method.

*Anal.* Subs., 0.1902, 0.1908: CO<sub>2</sub>, 0.6074, 0.6059; H<sub>2</sub>O, 0.1184, 0.1194. Calcd. for C<sub>21</sub>H<sub>20</sub>O: C, 87.45; H, 7.00. Found: C, 87.09, 86.60; H, 6.96, 7.00.

**Benzylation of *m*-Cresol by the Claisen Method.**—11.4 g. of finely cut sodium was suspended in 125 g. of toluene and 54 g. of *m*-cresol added. The mixture reacted rapidly to form a white cheesy mass, the temperature being controlled by immersing the flask in cold water. After standing overnight 64 g. of benzyl chloride was added and the mixture refluxed on an oil-bath at 150° for five hours. When cooled, it was washed twice with water to remove the sodium chloride and the toluene distilled off. The residue was dissolved in 250 cc. of Claisen's alcoholic potash<sup>6</sup> and extracted with 200 cc. of petroleum ether in 50-cc. portions to remove any ether present. The potash solution was neutralized with 6 *N* hydrochloric acid and extracted with ether. The ether was removed and the residue fractionated: 125–140°, 8.5 g.; 140–160°, 34.5 g.; 160–230°, 12.5 g.

**3-Methylphenyl Benzyl Ether.**—The petroleum ether extract, containing the Claisen's ether, distilled at 280–290°, decomposing above 290°. At 5 mm. it boiled at 142–145° and crystallized into white platelets melting at 45–46°. These points vary somewhat from those given by Staedel<sup>7</sup> but his work was repeated, giving results identical with the above.

**2-Benzyl-3-methylphenol.**—The fraction 140–160° contained two isomers, one solidifying and the other remaining as an oil. These were separated by pressing the mass between filter papers, which absorbed the oily compound and it could then be extracted with ether. The ether extract gave an oil boiling at 153–155° (4 mm.) and solidifying into crystals melting at 46–47°, which proved to be 3-methyl-6-benzylphenol, identical with that prepared by the aluminum chloride condensation.

The crystals from this fraction, after being pressed between filter papers, were crystallized from petroleum ether, giving long, regular needles melting at 71–72° and boiling at 157–159° (5 mm.).

*Anal.* Subs., 0.1769, 0.2256: CO<sub>2</sub>, 0.5483, 0.6993; H<sub>2</sub>O, 0.1127, 0.1428. Calcd. for C<sub>14</sub>H<sub>14</sub>O: C, 84.8; H, 7.12. Found: C, 84.53, 84.53; H, 7.13, 7.08.

**3-Methyl-2,6-dibenzylphenol.**—The fraction 160–230° was a heavy yellow oil which, on standing, yielded a very small amount of crystalline material which proved to be the dibenzyl derivative obtained by the aluminum chloride method, 3-methyl-4,6-dibenzylphenol. The remainder of the oil did not solidify but after several distillations boiled at 216–218° (5 mm.). This compound was also prepared from the monobenzyl derivative, 2-benzyl-3-methylphenol, and benzyl chloride by the Claisen reaction.

*Anal.* Subs., 0.2145: CO<sub>2</sub>, 0.6869; H<sub>2</sub>O, 0.1335. Calcd. for C<sub>21</sub>H<sub>20</sub>O: C, 87.45; H, 7.00. Found: C, 87.33; H, 6.96.

**2-Benzyl-3-methylphenyl Benzyl Ether.**—In the formation of 3-methyl-2,6-dibenzylphenol from 3-methyl-2-benzylphenol by the Claisen method, a small amount of the corresponding Claisen ether was isolated. The method of condensation was exactly as described previously. The petroleum ether extract solidified as soon as the petroleum ether had evaporated. Recrystallized from alcohol, the ether formed fine yellowish needles melting at 71–73°.

<sup>6</sup> Claisen, *Ann.*, **442**, 224 (1924).

<sup>7</sup> Staedel, *ibid.*, **217**, 46 (1882).

*Anal.* Subs., 0.0804: CO<sub>2</sub>, 0.2568; H<sub>2</sub>O, 0.0505. Calcd. for C<sub>21</sub>H<sub>20</sub>O: C, 87.45; H, 7.00. Found: C, 87.10; H, 7.03.

**Bromine Derivatives.**—The calculated molecular quantities of bromine were added to the chloroform solutions of the benzylated cresols with vigorous reaction and copious evolution of hydrogen bromide. In most cases the bromine derivative solidified on evaporation of the chloroform. Petroleum ether and alcohol were both used as crystallizing agents but the better results were obtained with alcohol.

The 4,6-dibromo-3-methyl-2-benzylphenol and the 2,4-dibromo-3-methyl-6-benzylphenol were prepared also in good yields by treating the corresponding dibromocresolates<sup>4,5</sup> in toluene with benzyl chloride, refluxing at 150–160°, and extracting as in the benzylation of *m*-cresol, by the Claisen method. The benzylated products came down as solids upon evaporation of the ether extracts.

TABLE I  
BROMO DERIVATIVES

Derivation of benzylphenol	Crystal form and solvent	M. p., °C.	Bromine, %	
			Calcd.	Found
2,6-Dibromo-3-methyl-4-	Shiny tan leaflets from alc.	86–87	44.91	44.23, 44.25
2,4-Dibromo-3-methyl-6-	Fine felted needles from alc. or pet. ether	102–103	44.91	44.81
4,6-Dibromo-3-methyl-2-	White felted needles from alc.	106–107	44.91	44.75
2-Bromo-3-methyl-4,6-di-	White platelets from alc. or pet. ether	65–67	21.76	21.38

**Benzoyl Derivatives.**—Esterification was accomplished by the Schotten–Baumann reaction.

TABLE II  
BENZOATES OF BENZYLPHENOL DERIVATIVES

Benzoates of benzylphenol	Crystal form and solvent	M p., °C.	Carbon, %		Hydrogen, %	
			Calcd.	Found	Calcd.	Found
3-Methyl-4-	Rosets from pet. ether; thin plates from alc.	70–71	83.40	83.03	6.00	5.99
3-Methyl-6-	Fine needles from alc.	58–59	83.40	83.13	6.00	6.14
		B. p. (5 mm.) 215–220°				
3-Methyl-2-	Shiny platelets from alc.	71–73	83.40	83.20	6.00	5.95
3-Methyl-4,6-di-	Fine fluffy needles from alc. or pet. ether	88–89	85.67	85.13	6.17	5.89
3-Methyl-2,6-di-	Thick yellow oil	...	85.67	85.55	6.17	6.36
		B. p. (5 mm.) 235–240°				

### Summary

1. Meta-cresol was benzylated by the aluminum chloride and the Claisen methods, giving three monobenzyl and two dibenzyl derivatives.
2. Bromine and benzoyl derivatives of the benzylated cresols were prepared.
3. Two of the bromine derivatives were also prepared by benzylating known bromocresols, thus establishing the structures of the compounds.