

corresponding quinone, was hydrolyzed to diphenyldihydroxyquinone (polyporic acid).

3. In a similar manner atromentin dimethyl ether was produced from dianisylquinone, the condensation product of anisole and quinone.

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## ACTION OF AROMATIC ALCOHOLS ON AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE. VII. CONDENSATION OF BENZYL ALCOHOL WITH PARA-CRESOL

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Para-cresol and benzyl alcohol in the molecular ratio of 2 to 1 dissolved in petroleum ether and treated with 0.5 mole of aluminum chloride gave a condensation product which upon fractional distillation yielded 35% of crude mono and 36% of crude dibenzylated *p*-cresol. When the reactants were used in the ratio of 3 to 1, with the same amount of aluminum chloride, the yields were 53 and 30%, respectively. Crystallization of the monobenzylated *p*-cresol from petroleum ether in the cold gave transparent needles melting at 35–36°. The dibenzylated *p*-cresol did not crystallize.

These compounds were found to agree in properties with those prepared by Claisen<sup>1</sup> by the action of benzyl chloride on the sodium salt of *p*-cresol in toluene, except that he did not obtain the monobenzyl derivative in crystal form.

The 2-benzyl-4-methylphenol was easily soluble in dilute potassium hydroxide and when treated with the calculated amount of benzoyl chloride gave the ester. As was anticipated, the 2,6-dibenzyl-4-methylphenol was not soluble, even in strong potassium hydroxide, but formed a solid. This, however, treated with benzoyl chloride reacted to produce the ester.

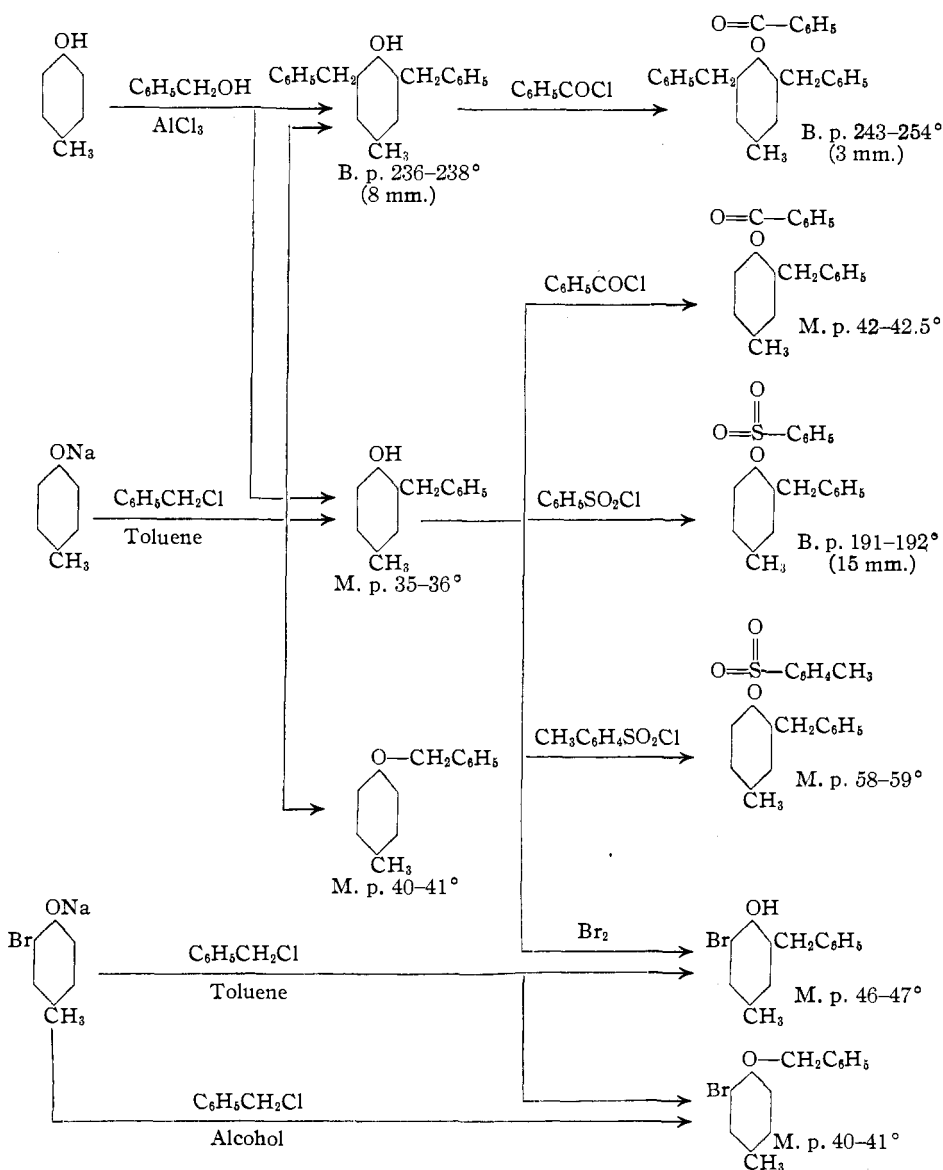
Bromination of 2-benzyl-4-methylphenol in chloroform gave 2-benzyl-4-methyl-6-bromophenol. This configuration was proved by preparing the same compound by benzylating 4-methyl-6-bromophenol by the Claisen reaction. In addition a small amount of 4-methyl-6-bromophenyl benzyl ether was obtained.

The monobenzylated *p*-cresol was further characterized by preparing benzene sulfonic and toluene sulfonic esters by the pyridine method.

### Experimental

**Benzyl Alcohol and *p*-Cresol with Aluminum Chloride.**—A mixture of 108 g. of *p*-cresol, 54 g. of benzyl alcohol and 75 g. of petroleum ether (40–60°) was placed in a tall cylinder and stirred mechanically while adding 33 g. of anhydrous aluminum chloride in small portions over a period of one hour. The temperature was kept below 30°.

<sup>1</sup> Claisen, *Ann.*, **442**, 210 (1925).



Hydrogen chloride gas was freely evolved. The mixture was allowed to stand overnight and then decomposed with ice and a little hydrochloric acid. The white oily product was extracted with ether. After distilling off the ether the residue was fractionated at 10 mm. The third fractionation gave:

Up to 100°	61.5 g. ( <i>p</i> -cresol)
165–185°	34.0 g.
185–250°	25.5 g.

The 165–185° fraction crystallized when seeded and placed in the cold. Recrystallization from petroleum ether gave transparent, prismatic crystals that melted at 35–36°.

*Anal.* Subs., 0.1508: CO<sub>2</sub>, 0.4695; H<sub>2</sub>O, 0.0980. Calcd. for C<sub>14</sub>H<sub>14</sub>O: C, 84.8; H, 7.12. Found: C, 84.93; H, 7.27.

From the 185–250° fraction there was isolated a portion which boiled at 236–238° (8 mm.). This was a viscous liquid that did not crystallize, and was assumed to be 2,6-dibenzyl-4-methylphenol.

*Anal.* Subs., 0.1732: CO<sub>2</sub>, 0.5553; H<sub>2</sub>O, 0.1068. Calcd. for C<sub>21</sub>H<sub>20</sub>O: C, 87.45; H, 6.99. Found: C, 87.41; H, 6.63.

**Preparation of 2-Benzyl-4-methylphenol, 2,6-Dibenzyl-4-methylphenol and 4-Methylphenyl Benzyl Ether by the Claisen Method.**—Using half molar quantities of *p*-cresol, sodium and benzyl chloride in three runs gave an average of 40 g. of 2-benzyl-4-methylphenol, m. p. 35–36°, and 11.8 g. of 2,6-dibenzyl-4-methylphenol, b. p. 236–238° (8 mm.). The petroleum ether extract from the above condensations gave an average of 6 g. of 4-methylphenyl benzyl ether, recrystallized from alcohol, m. p. 40–41°.

**Preparation of Benzoyl Esters.**—Employing the Schotten-Baumann reaction, 21 g. of 2-benzyl-4-methylphenol, 6.97 g. of potassium hydroxide in 20 cc. of water and 14.82 g. of benzoyl chloride gave a white oil which boiled at 205–206° (5 mm.). After long standing, it crystallized. Recrystallization from alcohol gave transparent plates, m. p. 42–42.5°.

*Anal.* Subs., 0.1008: CO<sub>2</sub>, 0.3056; H<sub>2</sub>O, 0.0541. Calcd. for C<sub>21</sub>H<sub>18</sub>O<sub>2</sub>: C, 83.4; H, 6.0. Found: C, 83.33; H, 6.03.

The 2,6-dibenzyl-4-methylphenol was treated with strong (50%) potassium hydroxide. The resulting solid was filtered off and treated with the calculated amount of benzoyl chloride. Heat was evolved and a yellowish oil was formed which was washed with dilute alkali and water, b. p. 243–245 (6 mm.).

*Anal.* Subs., 0.2300: CO<sub>2</sub>, 0.7200; H<sub>2</sub>O, 0.1342. Calcd. for C<sub>23</sub>H<sub>24</sub>O<sub>2</sub>: C, 85.67; H, 6.168. Found: C, 85.35; H, 6.43.

**Preparation of Sulfonyl Esters.**—By the pyridine method, 5 g. of 2-benzyl-4-methylphenol, 12.5 g. of pyridine and 4.5 g. of benzene sulfonyl chloride gave a viscous yellowish-red liquid, that boiled at 190–192° (2 mm.) and did not solidify.

*Anal.* Subs., 0.1029: BaSO<sub>4</sub>, 0.0739. Calcd. for C<sub>20</sub>H<sub>18</sub>SO<sub>3</sub>: S, 9.47. Found: S, 9.86.

By the same method, 5 g. of 2-benzyl-4-methylphenol, 12.5 g. of pyridine and 4.8 g. of toluene sulfonyl chloride gave a crystalline product. Recrystallization from petroleum ether gave transparent rhombohedra, m. p. 58–59°.

*Anal.* Subs., 0.1000 g.: BaSO<sub>4</sub>, 0.0676. Calcd. for C<sub>21</sub>H<sub>20</sub>SO<sub>3</sub>: S, 9.1. Found: S, 9.28.

**Preparation of the Monobromo Derivative.**—Addition of the calculated weight of bromine to 15 g. of 2-benzyl-4-methylphenol dissolved in chloroform produced 2-benzyl-4-methyl-6-bromophenol. Crystallization from about 85% alcohol gave a white silky felt-like product melting at 46–47°.

*Anal.* Subs., 0.1000: cc. of 0.1 *N* AgNO<sub>3</sub>, 3.6. Calcd. for C<sub>14</sub>H<sub>13</sub>OBr: Br, 28.84. Found: 28.771.

One-half mole of 6-bromo-*p*-cresol dissolved in toluene and treated with sodium and benzyl chloride by the Claisen method gave a product identical in crystal form and melting point with that obtained by brominating 2-benzyl-4-methylphenol.

From the petroleum ether extract in the above condensation there was isolated a small amount of 4-methyl-6-bromophenyl benzyl ether. Crystallization from strong alcohol gave transparent rhombohedra, m. p. 40–41°.

*Anal.* Subs., 0.1015: cc. of 0.1 *N* AgNO<sub>3</sub>, 3.68. Calcd. for C<sub>14</sub>H<sub>13</sub>OBr: Br, 23.84. Found: Br, 29.03.

### Summary

Para-cresol was benzylated by both the Claisen and the aluminum chloride methods and the yields were compared.

Bromination of 2-benzyl-4-methylphenol gave 6-bromo-2-benzyl-4-methylphenol, which was also prepared from 6-bromo-4-methylphenol by the Claisen reaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

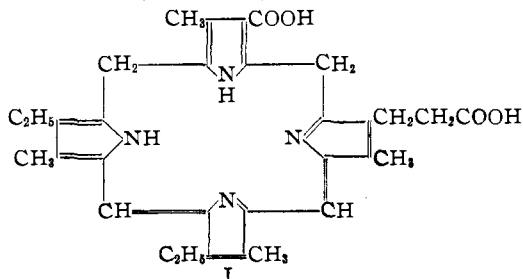
## STUDIES IN THE CHLOROPHYLL SERIES. V. THE STRUCTURE OF CHLOROPHYLL A

BY J. B. CONANT, EMMA M. DIETZ, C. F. BAILEY AND S. E. KAMERLING

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The experiments reported in the fourth paper of this series<sup>1</sup> indicated that chlorophyll *a* and the closely related compound phaeophorbide *a* contained the grouping  $-\text{CHOH}-\text{C}\begin{smallmatrix} \text{O} \\ // \\ \text{O} \end{smallmatrix}$ . In allomerization or "phase test saponification," we supposed that this structure was transformed into the  $\alpha$ -ketonic acid grouping which was subsequently easily removed as potassium oxalate by boiling the compounds with alkali. The resulting simple chlorin, chlorin *f*, was thus to be regarded as a partially hydrogenated rhodoporphyrin. It was uncertain whether the two hydrogen atoms which were removed from the secondary alcohol group were transferred to some other molecule or intra-molecularly to a pyrrole ring. A further study<sup>2</sup> has shown that the first alternative is correct and that the dehydrogenating agent is oxygen of the air. The structure of chlorin *f* is therefore that of a dihydrorhodoporphyrin (I); this formula replaces



<sup>1</sup> THIS JOURNAL, 53, 359 (1931). For other papers of this series see *ibid.*, 51, 3668 (1929); 52, 1233, 3013 (1930).

<sup>2</sup> A brief statement of these results was given in a letter to the editor, THIS JOURNAL, 53, 1615 (1931). The corresponding experiments are recorded in this present paper except for the study of the phase test, which will form a separate paper by Miss C. C. Steele.