

mixed benzoin. Benzoin itself as starting material gave benzoin as the end product.

2. An expeditious method for the preparation of α -aminobenzylphenylcarbinols is the catalytic reduction of the oximes of benzoin.

3. α -Aminobenzyl phenyl ketones are produced by the oxidation of α -aminobenzylphenylcarbinols.

4. α -Acetaminobenzyl phenyl ketones are produced by the oxidation of α -acetaminobenzylphenylcarbinols. The acetyl group may be removed by hydrolysis.

5. In the catalytic reduction of 2-chloro- α -hydroxybenzyl-4-methoxyphenyl ketoxime, the chlorine is largely split from the nucleus.

TUCKAHOE, NEW YORK

RECEIVED JULY 13, 1933
PUBLISHED OCTOBER 6, 1933

[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Action of Aromatic Alcohols on Aromatic Compounds in the Presence of Aluminum Chloride. VI. Condensation of Phenylpropylcarbinol and α -Chlorobutylbenzene with Phenol

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The work here described may be considered a continuation of that with Lewis and Grotemut¹ on the condensation of secondary alcohols with phenols.

The phenylpropylcarbinol used was prepared from propyl bromide and benzaldehyde by the Grignard reaction. A yield of 81% was obtained when the reactants were used in the proportion of one of propyl bromide to one of magnesium to four-fifths of benzaldehyde^{2,3} and when the reaction mixture was cooled to a slight visible reaction during the preparation of the Grignard reagent and in ice during the addition of the benzaldehyde.⁴ Because of the lack of agreement⁵ as to the boiling point and density of this compound these constants were carefully redetermined: b. p. 94–96° (6 mm.), sp. gr. 18/4°, 0.974.

Condensation of one mole of phenylpropylcarbinol (or α -chlorobutylbenzene) with one mole of phenol in petroleum ether at 20–25°, by means of one-half mole of aluminum chloride,⁶ gave a 20% yield of 4-(α -phenylbutyl)-phenol and a 6% yield of 2-(α -phenylbutyl)-phenol. These were separated by repeated fractionation at reduced pressure. Solution of the crude

(1) Huston, Lewis and Grotemut, *THIS JOURNAL*, **49**, 1365 (1927).

(2) Meisenheimer, *Ann.*, **442**, 180 (1925).

(3) Gilman and McCracken, *THIS JOURNAL*, **45**, 159 (1923).

(4) Rheinboldt and Roleff, *J. prakt. Chem.*, **109**, 175 (1925).

(5) Marshall and Perkin, *J. Chem. Soc.*, **59**, 885 (1891); Grignard, *Chem. Centr.*, **11**, 7622 (1901); Klages, *Ber.*, **37**, 2312 (1904); Puyal and Montague, *Bull. soc. chim.*, **27**, 857 (1920); Strauss and Grindel, *Ann.*, **439**, 276, 312 (1924).

(6) Huston, *THIS JOURNAL*, **46**, 2777 (1924).

product in Claisen's alcoholic potassium hydroxide and extraction with petroleum ether gave no evidence of the formation of α -phenylbutyl phenyl ether (see table).

Condensation of α -chlorobutylbenzene⁷ with phenol by Claisen's method⁸ gave a 13% yield of 2-(α -phenylbutyl)-phenol, a 12% yield of phenylbutylene⁹ and a 10% yield of α -phenylbutyl phenyl ether. The last two products were obtained by fractionation of the petroleum ether extract of the alcoholic potassium hydroxide solution.

Bromination of 4-(α -phenylbutyl)-phenol in cold chloroform with two moles of bromine gave 4-(α -phenylbutyl)-2,6-dibromophenol. This was also produced by condensing phenylpropylcarbinol with 2,6-dibromophenol by means of aluminum chloride.

The preparation of 2-(α -phenylbutyl)-4,6-dibromophenol was effected either by bromination of the substituted phenol or from 2,4-dibromophenol by the Claisen reaction.

Esters were prepared by the pyridine method.¹⁰

TABLE I

| Compound | | Physical appearance | | | | | |
|--|-------------------------------|---|-------|-------|-------------|-------|-------|
| 4-(α -Phenylbutyl)-phenol | | Mats of fine silky threads from pet. ether. (Shows tendency to swell and retain solvent) | | | | | |
| 2-(α -Phenylbutyl)-phenol | | Viscous oil | | | | | |
| α -Phenylbutyl phenyl ether | | Mobile colorless liquid (sp. gr. at 25°/4° 1.0067, n_{20} 1.5507) | | | | | |
| 4-(α -Phenylbutyl)-2,6-dibromophenol | | Viscous oil | | | | | |
| 2-(α -Phenylbutyl)-4,6-dibromophenol | | Viscous oil | | | | | |
| Benzoyl ester of 4-(α -phenylbutyl)-phenol | | Monoclinic crystals | | | | | |
| Empirical Formula | M. p. or b. p., °C. | Carbon, % | | | Hydrogen, % | | |
| | | Calcd. | Found | Found | Calcd. | Found | Found |
| C ₁₆ H ₁₈ O | M 49-50; B 154-155 (6 mm.) | 84.91 | 84.89 | 84.64 | 8.02 | 7.97 | 7.94 |
| C ₁₆ H ₁₈ O | B 144-146 (6 mm.) | 84.91 | 84.61 | 84.70 | 8.02 | 8.025 | 8.065 |
| C ₁₆ H ₁₈ O | B 123-125 (6 mm.) | 84.91 | 84.77 | 84.76 | 8.02 | 8.01 | 7.96 |
| C ₁₆ H ₁₆ OBr ₂ | B 188-189 (6 mm.) | Br, 41.63 | 41.49 | | | | |
| C ₁₆ H ₁₆ OBr ₂ | B 184-185 (6 mm.) | Br, 41.63 | 41.36 | | | | |
| C ₂₃ H ₂₂ O ₂ | M 70-71 | 83.58 | 83.4 | | 6.71 | 6.76 | |

The benzoyl, benzene sulfonyl and *p*-toluene sulfonyl esters of 2-(α -phenylbutyl)-phenol were heavy oils which failed to crystallize.

EAST LANSING, MICHIGAN

RECEIVED JULY 17, 1933
PUBLISHED OCTOBER 6, 1933

(7) This was prepared from the pure alcohol. It boiled at 73-75° (6 mm.) and had a sp. gr. at 18/4° 1.0182. Cf. Klages, *Ber.*, **37**, 2312 (1904).

(8) Claisen, *Ann.*, **442**, 210 (1925).

(9) Radziszewski, *Ber.*, **9**, 260 (1876).

(10) Einhorn and Holland, *Ann.*, **301**, 95 (1898).