

64. On the Alkylation of Phenol with Primary Alcohols in the Presence of Aluminium Chloride.

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With the view to introduce a normal alkyl side-chain into the aromatic, esp. phenolic, nucleus^{1) 2) 3)} we have investigated the reaction between the phenol and the alcohol in the presence of anhydrous AlCl_3 in the following three ways:

1) The alcohol- AlCl_3 equimolecular complex had been previously prepared and was then treated with phenol and AlCl_3 : the condensation without the additional AlCl_3 at 100°C . gave no reaction product, but at 150°C . gave 4% of n-butyl-phenol. The reaction with an addition of 1.0 mol. AlCl_3 at $120\text{--}130^\circ\text{C}$, 150°C . gave 24.0, 35.7% of n-butyl-phenol respectively.

2) The phenol- AlCl_3 equimolecular complex had been previously prepared and was then condensed with alcohol in the presence of AlCl_3 at $120\text{--}130^\circ\text{C}$ for one hour: the reaction with 0.0, 0.5, and 1.0 mol. of the additional AlCl_3 yielded trace, 21.2%, and 15.1% of n-butyl-phenol, respectively.

3) The condensation between the previously prepared alcohol- and phenol- AlCl_3 complex in the presence of AlCl_3 at $120\text{--}130^\circ\text{C}$ for several hours: the reaction with 0, 0.5 and 1.0 mol. of additional AlCl_3 gave 15.0, 36.7 and 23.3% of n-butyl-phenol, respectively.

The structure of the alkyl chain introduced by this method is confirmed from the consideration of the following facts: the butyl-phenol fractions obtained, b. p. $_{10}$ $110\text{--}113^\circ\text{C}$. and b. p. $_{10}$ $124\text{--}129^\circ\text{C}$. (o-isomer: b. p. $_{10}$ 110°C .⁴⁾; p-isomer:

b. p. $_{10}$ $125\text{--}126^\circ\text{C}$.⁴⁾) are both liquid, and the benzoate derivative of the p-isomer (b. p. $_{10}$ $124\text{--}128^\circ\text{C}$.) melts at $26.5\text{--}27.0^\circ\text{C}$. (m. p. 27°C .⁴⁾). On the other hand, sec- and tert-butylphenol are crystals (m. p. 55°C . and 99°C . respectively).

Literatures

- 1) Ipatieff; J. Org. Chem., **5**, 253 (1940).
- 2) Tsukervanik; J. Gen. Chem., **7**, 623 (1937); C. A. **31**, 6778 (1937).
- 3) Smith; J. Amer. Chem. Soc., **56**, 1419 (1934).
- 4) Sandulesco; Bull. Soc. Chim., (4) **47**, 1300 (1931).

65. Catalytic Dehydrogenation of Aliphatic Primary Alcohol. (II)

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In the foregoing report on the investigation of dehydrogenation of isoamyl-alcohol over Cu, $\text{CuO-Cr}_2\text{O}_3$ and $\text{Cu-Cr}_2\text{O}_3$ catalysts, we concluded that these