

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

Haruo Shingu and Hideo Matsushita.

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)

Haruo Shingu and Toyoji Tsuchihara.

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

catalysts could not retain their activities more than 15–20 hrs. and their industrial application would be impossible. (H. Shingu, T. Tsuchihara: Reports of the Institute for Chemical Research, Kyoto University, 18, 65 (1949)).

We studied further the catalytic dehydrogenation of aliphatic primary alcohol by passing the gaseous mixture of air and isoamyl, octyl and lauryl alcohol respectively over a copper gauze catalyst activated by silver, and the catalyst was found to be effective for a long duration and prospective for the industrial application. Upon the investigation of the influence of air–alcohol ratio, space velocity of the alcohol, the reaction temperature and the life of the catalyst, we obtained the best results when the alcohol and the air, the amount of the latter being 80–100% of that quantity necessary for the oxidation of the alcohol to the corresponding aldehyde, were passed over the catalyst at 340°–360°C. Generally speaking, the space velocity of the alcohol were found to influence little on the yield of aldehyde, within the range of our experiment (0.30–0.98/cc. hr.), only a slight decrease of yield was observed at the large space velocity. In the optimal conditions the conversion of isoamyl–alcohol was 55.3 mol%, the yield of aldehyde 44.0 mol % of the theoretical value based upon the amount of alcohol passed over the catalyst, or the selectivity for the aldehyde production 82.7%, and the yield of high boiling products 5.8% by weight. The catalyst retained its activity unchanged after the use for 55 hrs.

We confirmed further that this method, being conducted under reduced pressure, was as much effective for the octyl and lauryl alcohol as for the isoamyl alcohol as described above.

66. Study on the Preparation of Vanillin from Lignin.

Yusaku Fukuda.

The purpose of this study is to clarify the theory of kraft pulping process as well as the practical problem of obtaining vanillin from waste lignin.

Alkali lignin and thiolignin were oxidized by heating with nitrobenzene in the presence of caustic alkali under the conditions as suggested by Freudenberg and the yield of vanillin from two sorts of lignin were compared with each other.

About 15 g of alkali lignin prepared from wood powder of red pine, was heated for 3 hrs. at 160°C with nitrobenzene (35 cc) and 2N–NaOH solution (600 cc) in an autoclave. After removal of excessive nitrobenzene and aniline by means of steam distillation, the reaction mixture was extracted with ether repeatedly. Vanillin in the extract was determined by converting it into *m*-nitrobenzohydrazone.

The yield of vanillin was found to be 10.5% based upon the lignin used in