[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

The Migration of Alkyl Radicals. The Scission of a Tertiary Octyl Group

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In a previous report[2] the migration of alkyl groups from phenolic nuclei to the benzene ring was shown. In the migration of the octyl group, 1,1,3,3-tetramethobutyl, the group did not migrate as such but underwent scission into butyl groups. In this communication the results of this scission are applied to additions to the phenolic nucleus. Means of preparation of *p*-*t*-butyl phenol are thus afforded.

In the first experiment 4-(1,1,3,3)-tetramethobutylphenol (I) was treated with anhydrous aluminum chloride in the presence of phenol. The products were *t*-butylphenol (II) and phenol; there was some unreacted (I). The reaction appears to consist of cleavage and scission of the octyl group with subsequent additions of the C_4 segments. The use of aluminum chloride in these three types of chemical action is well established.

(I) is prepared commercially by the condensation of diisobutylene and phenol. The obvious thought is to perform this condensation under the more vigorous conditions which convert (I) to (II). This was done and excellent yields of (II) were obtained.

Procedure

(I) **The Action of 4-(1,1,3,3)-Tetramethobutylphenol and Phenol in the Presence of Aluminum Chloride.**—Molar quantities of phenol and (I) were melted to homogeneity and a two and a third molar quantity of anhydrous aluminum chloride added in small quantities. (The quality of aluminum chloride was found to affect the amount required; that given is for the most impure "technical" grade used. With very good, white, resublimed material, a 0.01 molar amount gave a good yield of product.) Hydrogen chloride and heat are evolved during the addition. After the addition, the whole was heated with occasional stirring for ten hours on a steam-bath. The product was cooled and hydrolyzed with ice and hydrochloric acid. The liquid layer was separated, washed and dried with sodium sulfate. Fractional distillation yielded (II) b. p. 230–233°, m. p. 84–86°. One recrystallization from diisobutylene yielded a product, m. p. 99°, in yields up to 75% based on the amount of unreacted octylphenol recovered (12%, b. p. 275–285°, m. p. 78°). The products were identified by mixed melting points with known samples.

(II) **The Action of Phenol, Diisobutylene, and Aluminum Chloride.**—A one and a third molar quantity of aluminum chloride was added in small quantities to a mole of phenol. The resulting product was heated on a steam-bath and half a mole of diisobutylene slowly added by means of a funnel whose opening extended beneath the surface of the reaction mixture. The whole was heated for six hours after the addition. Hydrolysis and subsequent isolation of products were performed as in the first procedure. (II) was obtained in 67% yield, (I) in 14% yield. The ratio of (I) and (II) can be thrown almost completely in either direction by varying the reaction conditions; less vigorous conditions favor (I).

Summary

1. A further study of the cleavage of the (1,1,3,3)-tetramethobutyl group has been made.

2. *t*-Butylphenol has been prepared from 4-(1,1,3,3)-tetramethobutylphenol and phenol.

3. *t*-Butylphenol has been prepared from diisobutylene and phenol.

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[2] Smith, THIS JOURNAL, 59, 899 (1937).