[CONTRIBUTION FROM THE UNIVERSITY OF NOTRE DAME]

THE CATALYTIC CONDENSATION OF ACETYLENE WITH BENZENE AND ITS HOMOLOGS

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The Preparation of Diphenylethane

Unsymmetrical diphenylethane has been prepared[1] by the condensation of benzene with paraldehyde in the presence of concd. sulfuric acid. It has been demonstrated that acetylene may be substituted for acetaldehyde in the preparation of quinaldine[2] and the acetals.[3] The method described in this paper consists in the similar substitution of acetylene for acetaldehyde in the preparation of diphenylethane from benzene and paraldehyde according to Baeyer. This synthesis may in a general way be represented by the equation, $C_2H_2 + 2C_6H_6 \longrightarrow CH_3CH(C_6H_5)_2$. Acetylene does not combine with benzene directly as indicated in this equation. However, when acetylene is passed into a mixture of benzene and concd. sulfuric acid in the presence of a mercury salt as a catalyst, the condensation of acetylene and benzene into diphenylethane is readily effected.

Experimental Part.—A mixture of 500 cc. of benzene, 50 cc. of concd. sulfuric acid and 5 g. of mercuric sulfate was put into a flask fitted with a 2-hole stopper, one hole of which was closed with a glass rod, the other fitted with a glass tube bent at a right angle. The flask was then tared and connected with a gasometer containing acetylene under a pressure of about 1.5 meters of water. The acetylene was washed through concd. sulfuric acid. The system was swept free from air by removing the glass rod from the stopper. The absorption of acetylene took place quite rapidly with the evolution of considerable heat. The flask was cooled by immersion in ice water. The absorption was continued until approximately three-fourths to four-fifths of the calculated amount of acetylene had been absorbed. During the absorption the reaction mixture turned first yellow and then brown. With the proper cooling there was little evidence of the formation of tarry or solid products. The absorption was completed in from two and one-half to three hours. To isolate the products, the reaction mixture was diluted with four times its volume of water and neutralized with sodium carbonate. The emulsion which formed upon the addition of sodium carbonate was broken by heat and the addition of common salt, or by extraction with ether. The two layers were then separated, and the upper layer which contained the hydrocarbons was subjected to a fractional distillation. Between 75° and 105° some unchanged benzene distilled. The temperature rose rapidly to 250° when diphenylethane commenced to distil. There was no evidence of decomposition until the temperature reached about 340°. By repeated fractionation diphenylethane was obtained; b. p., 268–272°. From the higher-boiling fraction a small amount of dimethylanthracene hydride was obtained. This product is formed by the condensation of two molecules of acetylene with two molecules of benzene. A yield of 40 to 50% of the calculated amount of diphenylethane referred to the amount of acetylene absorbed was obtained. The best yields were obtained when the reaction

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[1] Baeyer, *Ber.*, **7**, 190 (1874).

[2] Nieuwland and Vogt, THIS JOURNAL, **43**, 2671 (1921).

[3] Reichert, Bailey and Nieuwland, *ibid.*, **45**, 1552 (1923).

was allowed to take place at 10° to 20°. When the reaction took place without being cooled, the heat of reaction raised the temperature of the mixture up to 60° or 70°. Under these conditions the acetylene was absorbed even more rapidly but the yield of diphenylethane was thereby greatly reduced and instead of diphenylethane, products of a solid character were obtained. When the reaction was allowed to take place at higher temperatures there was evidence of the formation of sulfur dioxide also. It was thought possible that under the influence of the reduced mercury which is formed in small quantities in the reaction, the sulfuric acid might have oxidized the diphenylethane to benzophenone or the dimethylanthracene hydride to anthraquinone. These substances were, however, not found among the products of the reaction.

The Preparation of the Homologs of Diphenylethane

Baeyer's method for the preparation of diphenylethane was applied by Fischer[4] to the preparation of ditolylethane, namely, the condensation of toluene with paraldehyde in the presence of sulfuric acid. The process described in this paper consists in the substitution of acetylene for acetaldehyde in Fischer's method for the preparation of ditolylethane. Anschütz,[5] who prepared diphenylethane and ditolylethane by the action of ethylidene chloride on benzene and toluene, respectively, likewise prepared dixylylethane by the same method. No reference was found in the literature to the preparation of dimesitylethane or ethylidene *bis*-ethylbenzene.

The method just described for the preparation of diphenylethane was found applicable to the preparation of its homologs. With toluene a 45 to 50% yield of ditolylethane (b. p., 295–300°), together with a small yield of tetramethylanthracene hydride was obtained. Xylene yielded 50 to 55% of dixylylethane (b. p., 322–326°) and a small amount of a high-boiling fraction, probably hexamethylanthracene hydride. Mesitylene, prepared by the condensation of acetone according to Bender and Erdmann, yielded 18 to 20% of dimesitylethane; b. p., 344–348°. The absence of a high-boiling fraction in this case coincides with the fact that the condensation of two molecules of acetylene with two molecules of mesitylene to form octamethylanthracene hydride is theoretically impossible. Ethyl benzene, prepared from ethyl bromide and bromobenzene according to Gattermann, yielded 20 to 25% of ethylidene *bis*-ethylbenzene, and a small amount of a high-boiling fraction, probably dimethyldiethylanthracene hydride. Both dimesitylethane and ethylidene *bis*-ethylbenzene are fluorescent and like their homologs boil without decomposition.

Summary

A new and practical method for the preparation of diphenylethane, ditolylethane and dixylylethane is described. This method consists in the condensation of acetylene with benzene, toluene and xylene, respectively, in the presence of concd. sulfuric acid and a mercury salt.

This method has been applied to the preparation of the two compounds, dimesitylethane and ethylidene *bis*-ethylbenzene.

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[4] Fischer, *Ber.*, **7**, 1193 (1874).

[5] Anschütz, *Ann.*, **235**, 326 (1886).