[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Condensation of Acetic Acid and Cyclohexene in the Presence of Boron Fluoride

BY H. L. WUNDERLY AND F. J. SOWA

The purpose of this study was to determine the effect of boron fluoride upon the formation of cyclohexyl acetate from cyclohexene and acetic acid.[1] A series of reactions was carried out at constant temperature with a variation in the percentage of boron fluoride and the time of reaction.

Experimental Part

The experimental procedure for all reactions was the same as that described below. The boron fluoride was used in the form of the acetic acid–boron fluoride compound which was prepared according to the method of Bowlus and Nieuwland.[2] The acetic acid and acetic acid–boron fluoride compound were weighed into a 250-cc. glass bottle. The percentage of boron fluoride used was calculated on the basis that the sum of the weight percentages of acetic acid and of boron fluoride was equivalent to 100%. One-third of a mole of cyclohexene,[3] b. p. 82°, distilled twice through a 45-cm. Widmer column, was weighed separately and then added to the acetic acid–boron fluoride mixture in the glass bottle. The reaction bottle was sealed and immediately put into a thermostatically regulated oil-bath kept at a temperature of 80 ± 0.5°. The reaction time was varied from fifty to two hundred and twenty hours. Upon the elapse of time the reaction bottle was removed from the bath and cooled to room temperature. Then the bottle was opened and the contents weighed in order to check whether any loss due to leakage had occurred. The mixture was neutralized with saturated sodium carbonate solution and the upper layer separated (all residues were collected in ether and added to the upper layer). After the ester and cyclohexene layer was washed with water and dried over calcium chloride the mixture was fractionated carefully and the fraction boiling at 175° was collected as the ester. Upon the removal of the ester fraction the temperature rose rapidly and the distillation was discontinued. The quantity of residue varied from 1.5 to 8.9 g. depending upon the quantity of boron fluoride used. The following yields for the varying amounts of boron fluoride, substantially unchanging with time, were obtained. The apparent equilibria were plotted against the percentage boron fluoride as shown in Fig. 1.

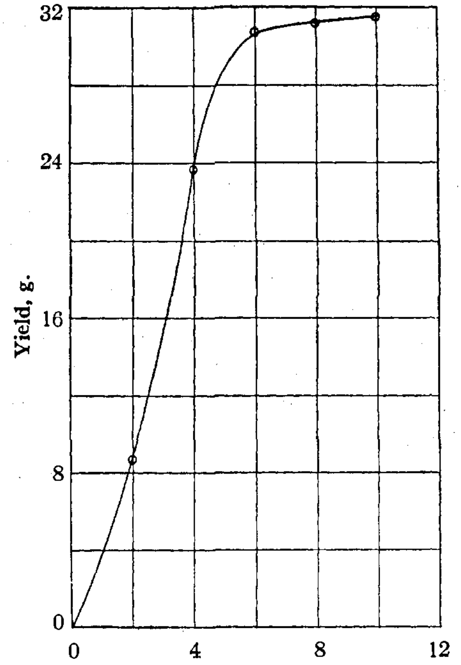

Fig. 1.

TABLE I

BF_3, %	2	4	6	8	10	15	18
Yield, g.	8.1–8.8	23.5–23.8	30.7–31	31.3	31.6	31.9[a]	29.3[a]

[a] Diminishing slowly with time.

The solubility of boron fluoride in cyclohexyl acetate was determined by slowly passing boron fluoride into 0.868 mole of the ester. After a period of eleven hours it was found that 0.882 mole of the boron fluoride was absorbed. Heat was liberated during the absorption of the boron fluoride; however, as the quantity of boron fluoride reached a mole per mole ratio with the ester the mixture gradually cooled to room temperature. The absorption also became extremely slow as the molar ratio was reached.

Discussion

It had been noticed throughout the purifications that the quantity of residue obtained from the individual runs having concentrations of boron fluoride equivalent to 10% and less ranged between 1.5 and 1.9 g. Beyond these concentrations of boron fluoride the quantity of residue increased rapidly. This indicates that higher concentrations of boron fluoride rapidly effects polymerization. In addition it was found that one mole of boron fluoride was absorbed by one mole of cyclohexyl acetate. Thus when a sufficient quantity of ester was produced with the lower concentrations of boron fluoride the boron fluoride was made inactive by absorption in the ester. Thereupon the yield of ester remained constant for that particular percentage of boron fluoride giving the appearance of an equilibrium. As higher percentages of boron fluoride were used

---

(1) Brunel, *Ann. chim. anal.*, [8] **6**, 216 (1905).

(2) Bowlus and Nieuwland, THIS JOURNAL, **53**, 3835 (1931).

(3) Dehn and Jackson, *ibid.*, **55**, 4285 (1933).

these equilibria approached one another until a maximum was reached. Beyond this point polymerization occurred with a prolongation of reaction time and the yield of ester subsequently decreased.

An explanation for this gradual approach to a maximum is offered on the basis of the following considerations: that the concentration of boron fluoride necessary for bringing about a reverse of the condensation reaction having a reaction velocity equal to that of the condensation reaction, is greater than that used for the condensation itself. Thus in those reactions where low concentrations of boron fluoride are used a state is reached in which the boron fluoride is absorbed by the ester and the concentrations are not sufficient to effect a reversal having a velocity equal to the condensation velocity. As the concentration of boron fluoride is increased in the ester the velocity of the reverse reaction is increased. When the proper amount of boron fluoride is present the velocity of the reverse reaction is equivalent to the velocity of the condensation reaction: there being sufficient boron fluoride on both sides of the reaction to cause the reverse and condensation reactions to proceed with equal velocities. Beyond this concentration of boron fluoride polymerization is more pronounced.

Summary

The influence of time and concentration of boron fluoride upon the condensation of acetic acid with cyclohexene at a constant temperature has been studied. The concentration of boron fluoride is shown to have a marked effect upon the quantity of ester obtained. An explanation was offered for the change in apparent equilibria with the quantity of boron fluoride used.

NOTRE DAME, INDIANA RECEIVED MARCH 11, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

Sulfur Studies. XI. Some Sulfur Derivatives of Benzaldehyde

BY J. H. WOOD AND R. W. BOST

Practically nothing is known about monomeric thioaldehydes since they polymerize immediately upon formation. However, the conditions under which they are formed profoundly influence the nature of the resulting polymerization and we have found that reactions by which one would expect to obtain monomeric thiobenzaldehyde lead to a variety of compounds such as the thioester, the mercaptan, the dithio acid, the disulfide, the cyclic trimer, and other polymers. It is the purpose of this paper to describe some of these reactions and to offer a mechanism for the formation of some of the compounds obtained.

Benzal chloride and sodium sulfide react in alcoholic solution to form monomeric thiobenzaldehyde, C_6H_5CHS. However, the compound cannot be isolated and it immediately undergoes polymerization or side reactions. A part polymerizes to β-trithiobenzaldehyde. Some undergoes the Cannizzaro reaction to give benzyl mercaptan, dithiobenzoic acid, and a small amount of benzyldithiobenzoate. A portion of the mercaptan then reacts with thiobenzaldehyde to form a small quantity of benzyl mercaptal of benzaldehyde.

It has been suggested that the Cannizzaro reaction proceeds through ester formation. Our work confirms this belief. That is, thiobenzaldehyde readily undergoes polymerization to dithiobenzoate, and in the presence of alkalies such as sodium sulfide, the ester is saponified to the thio alcohol and dithio acid. On the other hand, the Cannizzaro reaction involving thiobenzaldehyde can be arrested at the ester stage provided that the monomer is formed under conditions which do not produce saponification of the ester. This is accomplished by depolymerizing β-trithiobenzaldehyde by distilling it at 3 mm. in the presence of a few drops of sulfuric acid. A part of the monomer in the distillate immediately re-polymerizes to the trimer and the rest polymerizes to the ester. The Cannizzaro reaction can then be completed from this point if desired by adding sodium sulfide whereupon the thio acid and thio alcohol are immediately formed.

While β-trithiobenzaldehyde is mainly depolymerized by distilling at low pressure in the presence of sulfuric acid, some decomposition also occurs with the formation of stilbene and sulfur. Some tetraphenylthiophene is also formed by the