CHEMISTRY

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Professor Ed F. Degering, Purdue University, was elected chairman of the section for 1946.

Synthesis and Reactions of Ketenes*

William A. Allen with Ed F. Degering, Purdue University

A recent study by Gwynn and Degering[1] has shown, for the first time, that many ketones react with ketene in the presence of concentrated sulfuric acid, and in each case the product was found to be the acetate of the enol form of the specific ketone employed. These workers studied the reaction of ketene with many ketones, and made a very detailed investigation of the reaction of ketene with acetone.

The subject of the present investigation is a study of the reaction of ketene with 2-butanone, using sulfuric acid as a catalyst. Optimum conditions for this condensation are presented.

Experimental

Materials Used. The acetone used for the generation of the ketene was obtained from Carbide and Carbon Chemicals Corporation and was over 99 per cent pure.

The methyl ethyl ketone used for the condensations with ketene was supplied by the Shell Chemical Company and had a boiling range of 79°C. to 80.5°C. This material was not subjected to further purification.

The sulfuric acid, used exclusively as a catalyst in this work, was the technical grade (66° Baume in every case), and was obtained from various sources.

Pyrolysis and Condensation. The ketene generator was constructed substantially as described by Hurd[2] and modified by Gwynn[1]. In order to remove the unreacted acetone from the gaseous mixture, the pyrolytic products were conducted first through two water-cooled condensers, and then through two cold traps, the first of which was maintained at 0° C. and the second at —35°C. to —40°C. The resultant, substantially acetone-free, gas was then run into the material with which the desired reaction was to be effected. This introduction was facilitated by means of a small inlet tube which directed the entering gases into the blades of a rapidly revolving stirrer which served to disperse the material into

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* Based upon a thesis submitted by William A. Allen to the faculty of Purdue University in partial fulfillment of the requirements for the Degree of Master of Science, May, 1942.

[1] Gwynn, B. H. and Degering, Ed. F., Condensation Products of Ketene with Ketones, J. Am. Chem. Soc., **64**, 2216 (1942).

[2] Hurd, J. Org. Chem., **5**, 122 (1940).

minute bubbles. The reaction tube was raised to the desired temperature by means of an externally heated oil-bath. An expansion chamber surrounded by an ice-bath was placed in a convenient position to return volatile liquids to the reaction chamber. The output of the generator was approximately 0.25 mole of ketene per hour. All analyses of products were made on a modified Podbielniak-type fractionating column, and the 2-buten-2-yl acetate obtained in this manner checked with the constants previously reported.[1]

Discussion

The reaction of ketene with 2-butanone was investigated for the purpose of determining optimum conditions for this condensation. The product, 2-buten-2-yl acetate, was previously prepared by Gwynn and Degering,[1] who condensed ketene with methyl ethyl ketone in the presence of sulfuric acid as a catalyst, and obtained a product which they

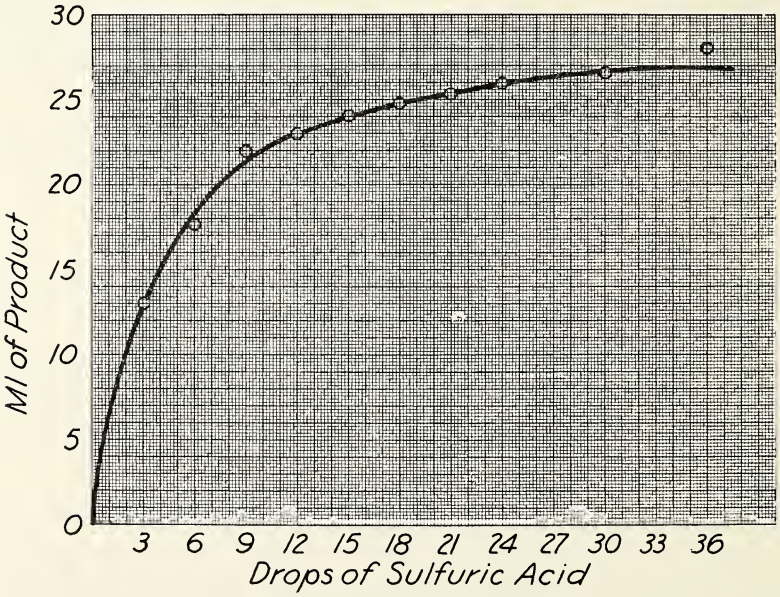

Figure 1

identified by several methods, including the determination of a saponification equivalent of the unsaturated ester and the formation of a 2,4-dinitrophenylhydrazone of the ketone obtained upon hydrolysis of the product. No attempt was made to determine the relative amounts of isomers obtained from this reaction.

According to expectation, a certain amount of ketene polymerization accompanies this reaction.

In determining the effect of catalyst concentration, the reaction time and reaction temperature were arbitrarily set at three hours and 75°C., respectively. The effect of varying the catalyst concentration is shown by Figure 1. Optimum results were obtained with a concentration of

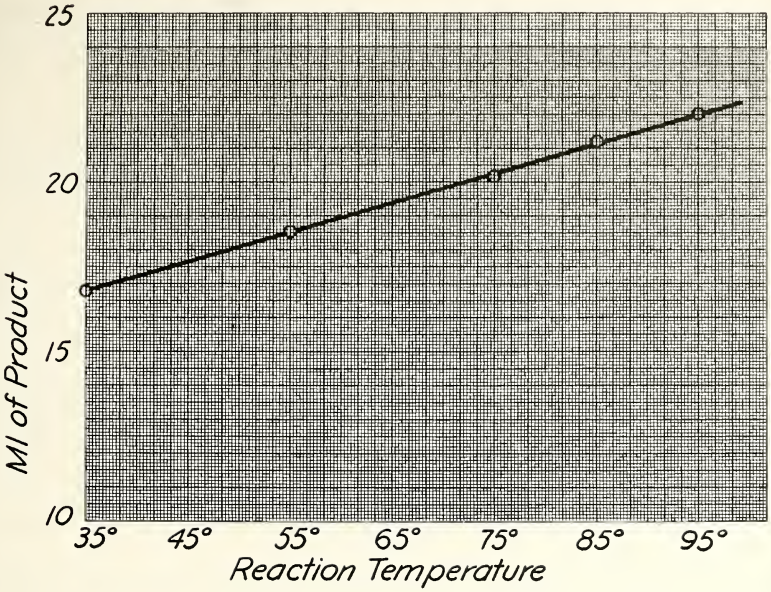

Figure 2

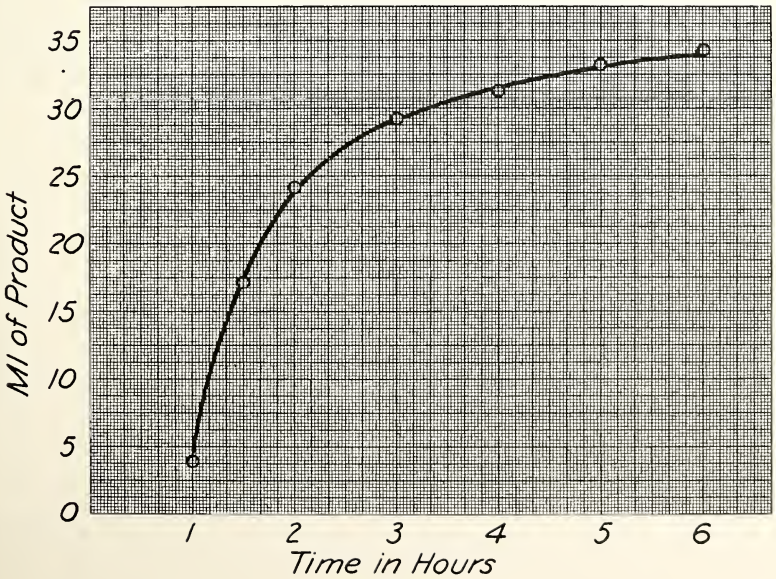

Figure 3

0.009 mole of sulfuric acid for each mole of 2-butanone. This optimum value may be calculated from Figure 1, which indicates that, under the experimental conditions, fifteen drops (0.5 milliliter) of sulfuric acid is the desired amount.

The effect of varying the bath temperature is shown by Figure 2. It will be seen that as the temperature is increased the yields of 2-buten-2-yl acetate are progressively increased, but due to operational difficulties which arise above 75°C., this temperature is taken to be optimum under the prevailing experimental conditions.

Figure 3 shows the effect of increasing the amount of ketene added to a given amount of methyl ethyl ketone. The amount of product increases quite rapidly for a time and then tends to approach a constant value. This fact may be brought about by a decrease in concentration of the methyl ethyl ketone which accompanies its utilization in the reaction. The optimum length of time for ketene passage was found to be approximately four hours, thus giving a value of one mole of ketene passed into the reaction mixture for 0.784 mole of methyl ethyl ketone employed.

Summary

A study has been made of the reaction between ketene and butanone to yield 2-buten-2-yl acetate. The optimum conditions determined for the reaction, as carried out on a batch scale, are with a rate of flow of 0.25 mole per hour of ketene through 0.784 mole of butanone in the presence of 0.007 mole of sulfuric acid at a temperature of 75°C. The conversion is about 39 per cent. No attempt was made to re-cycle the ketene and thus determine the overall yield. The polymerization of ketene is decreased by increasing the temperature of operation. Sulfuric acid was the most effective of the catalysts studied. The conversion of the butanone to 2-buten-2-yl acetate increases with the reaction time.