

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE UNIVERSITY OF MONTANA]

## THE ADDITION OF CHLOROFORM TO ALDEHYDES

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### Introduction

The addition of chloroform to aldehydes and ketones has been previously studied only to a limited extent. Willgerodt<sup>1</sup> and Guedras<sup>2</sup> have confined their studies to acetone. Eckley and Klemme<sup>3</sup> have shown that this addition will also take place with methylethyl ketone but not acetophenone. Jocicz<sup>4</sup> has studied the behavior of benzaldehyde under similar circumstances. Yoder<sup>5</sup> states that he prepared chloretone and trichloromethyl-phenyl carbinol from the corresponding ketone and aldehyde, respectively, by the addition of chloroform in the presence of alkali, but gives no experimental details.

This investigation has been made with a view of adding some data to those already existing concerning trichloromethyl-phenyl carbinol and to determine whether or not chloroform would condense with other aldehydes than benzaldehyde.

### Experimental Part

**Addition Reaction Studies.**—In order to find the best conditions for the reaction some ten different mixtures of chloroform, benzaldehyde and potassium hydroxide were tried under various conditions. Continuous mechanical stirring was found to be a great aid in shortening the time of the reaction. The following method gave the best results.

To a mixture of 33 g. of benzaldehyde and 60 g. of dry chloroform was added with constant stirring 4 g. of powdered potassium hydroxide over a half-hour period. The stirring was continued for 1.5 hour. Ether was added to the reaction mixture and the resultant mixture filtered. The ether and chloroform were removed by distillation from a steam-bath and the benzaldehyde by distillation under diminished pressure. The trichloromethyl-phenyl carbinol came over at 155–6° (150 mm.); yield, 11–12 g.;  $d_{20}^{20}$ , 1.464;  $n_{25}$ , 1.5672.

*Anal.* Calcd. for  $C_8H_7OCl_3$ : Cl, 47.18. Found: 47.15.

It is insoluble in water, but readily soluble in ether, ethyl alcohol, benzene, carbon tetrachloride, chloroform, carbon disulfide, toluene, methyl alcohol and acetone.

<sup>1</sup> Willgerodt, *Ber.*, **14**, 2451 (1881); **15**, 2305 (1882); **16**, 1585 (1883).

<sup>2</sup> Guedras, *Compt. rend.*, **133**, 1011 (1901).

<sup>3</sup> Eckley and Klemme, *THIS JOURNAL*, **46**, 1252 (1924).

<sup>4</sup> Jocz, *Chem. Centr.*, [5] **1**, 1013 (1897).

<sup>5</sup> Yoder, *THIS JOURNAL*, **45**, 475 (1923).

### Trichloromethyl-furan Carbinol

To a mixture of 33 g. of furfural and 60 g. of chloroform was added 4 g. of potassium hydroxide and the same procedure was followed as in the case of benzaldehyde. The trichloromethyl-furan carbinol boils at 115–118° (120 mm.); yield, 7–8 g.;  $d_{20}^{20}$ , 1.452;  $n_{25}$ , 1.5346.

*Anal.* Calcd. for  $C_6H_3O_2Cl_3$ : Cl, 49.37. Found: 48.95.

This compound darkens perceptibly in two to three hours, even when protected from the light. Hence it was necessary to analyze and test the sample as soon as possible. It is insoluble in water but soluble in acetone, methyl alcohol, toluene, carbon disulfide, chloroform, carbon tetrachloride, benzene, ethyl alcohol and ether.

An attempt was made to carry out this reaction with salicylaldehyde but no addition compound could be isolated.

In order to test this reaction with the aliphatic aldehydes, formaldehyde, acetaldehyde, propionic, butyric and *iso*-valeric aldehydes were used; 60 g. of chloroform in a flask surrounded by snow was saturated with formaldehyde gas and 4 g. of powdered potassium hydroxide added. On allowing the flask to warm gradually the formaldehyde rapidly polymerized, but no traces of the desired compound could be detected. Adding the potassium hydroxide to the chloroform before the saturation with formaldehyde also gave negative results. An attempt was also made to get this addition by heating chloroform, potassium hydroxide and paraformaldehyde in a sealed tube. The results were negative in so far as obtaining the desired product were concerned.

A similar set of experiments was tried with gaseous and para-acetaldehyde with like negative results.

In the cases of propionic, butyric and *iso*-valeric aldehydes the procedure developed for benzaldehyde was used. The products from propionic aldehyde gave negative tests for chlorine.

Both butyric and *iso*-valeric aldehydes gave mixtures of condensation products which gave positive tests for chlorine. But it was impossible to obtain either by use of volatility with steam or by fractionation under diminished pressure any fraction with sufficient percentage of chlorine even to approach a pure addition product.

### Summary

1. The addition compounds of chloroform with benzaldehyde and furfural have been prepared and studied.
2. Chloroform does not add to formaldehyde, acetaldehyde, propionic, butyric, *iso*-valeric or salicylic aldehydes.

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