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SOME ALCOHOLS CONTAINING THE TRICHLOROMETHYL GROUP

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Introduction

Two general methods have been used, in the past, in preparing alcohols containing the trichloromethyl group. One was the condensation of chloroform with aldehydes and ketones in the presence of potassium hydroxide. This has been shown to work for benzaldehyde[1] and furfural, but not for formaldehyde, acetaldehyde, propionic, butyric, *iso*valeric or salicylic aldehydes.[2] Only a limited number of ketones have been reported as tested up to this time. Willgerodt[3] and Guedras[4] have confined their studies to acetone. The product is now being manufactured in considerable amounts, for medicinal use, under the name chloretone. Ekeley and Klemme[5] have shown that this condensation also takes place with methylethyl ketone but not acetophenone. In connection with the present investigation the author has confirmed the findings of Ekeley and Klemme and found that unsatisfactory results are also obtained with diethyl ketone, dipropyl ketone, ethylpropyl ketone and methyl-*iso*butyl ketone.

The other method which has been used is to add chloral to an organomagnesium halide under the general procedure of the Grignard reaction. This has given satisfactory results in the preparation of trichloro-*iso*propyl alcohol,[6] known medicinally as isopral, but this seems to be the only case reported where this reaction has been used to prepare a member of this series.

In view of the limitations of the first method of preparation, the author has used the latter method in the present investigation and judging from the results obtained believes it to be of more general application.

Experimental Part

Preparation of the Alcohols.—The procedure followed was in general that of the Grignard reaction. The organomagnesium halides were prepared by treating 6g. portions of magnesium turnings with 32 g. of ethyl bromide, 34 g. of propyl bromide, and 35 g. of benzyl chloride, respectively; 37 g. of freshly distilled chloral in an equal volume of dry ether was slowly

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[1] Jocicz, *Chem. Centr.*, [5] Pt. **1,** 1013 (1897).

[2] Howard, THIS JOURNAL, **47,** 455 (1925).

[3] Willgerodt, *Ber.*, **14,** 2451 (1881); **15,** 2305 (1882); **16,** 1585 (1883).

[4] Guedras, *Compt. rend.*, **133,** 1011 (1901).

[5] Ekeley and Klemme, THIS JOURNAL, **46,** 1252 (1924).

[6] Henry, *Compt. rend.*, **138,** 205 (1904).

added to the ethereal solutions of the organomagnesium halides. The first half of the chloral reacted very readily, but it was necessary to warm the reaction mixture gently during the addition of the last half and then reflux for an hour and a half to complete the reaction. The resulting product was then decomposed with 2 *N* hydrochloric acid and the ether washed in turn with water, sodium bicarbonate solution, sodium bisulfate solution and water. It was dehydrated over anhydrous sodium sulfate, the ether removed by distillation and the alcohol distilled in a vacuum.

Preparation of the Esters.—The acetates were prepared by heating the alcohols with an excess of acetic anhydride for two hours at 130–135°.

The benzoates were prepared by treatment with benzoyl chloride according to the usual procedure of the Schotten-Baumann reaction.

The results are given in Table I.

TABLE I

RESULTS

	Substance	B. p., °C.	Mm.	Yield, g.
1.	Trichloromethyl-ethyl carbinol	99	680	13–14
2.	Trichloromethyl-propyl carbinol	115	686	10–11
3.	Trichloromethyl-benzyl carbinol	97	686	10–11

	Anal. for Cl, %		d_{20}^{20}	Acetate		Benzoate	
	Calcd.	Found		B. p., °C.	Mm.	B. p., °C.	Mm.
1.	59.93	60.01	1.488	164–165	680	217–218	680
2.	55.55	55.61	1.481	168–169	686	197–198	686
3.	44.42	44.31	1.365	159–160	686	210–211	680

The trichloromethyl-ethyl carbinol is soluble in water to about the extent of 2 g. in 100 cc. at 20°. The propyl compound is only very slightly soluble in water, while the benzyl compound is insoluble. All of these alcohols are readily soluble in ether, ethyl alcohol, benzene, carbon tetrachloride, chloroform, carbon disulfide, methyl alcohol and acetone.

Summary

Ethyl-, propyl-, and benzyl-trichloromethyl carbinols as well as their acetic and benzoic esters have been prepared and studied.

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