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

# SOME ESTERS OF TRIBROMOMETHYLPHENYLCARBINOL

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## Introduction

Tribromomethylphenylcarbinol was first prepared by Siegfried,[1] who gives no further experimental details than to state that he used the method of Jocitsch[2] to prepare the analogous chlorine compound. The author[3] has already submitted an improved method for the preparation of trichloromethylphenylcarbinol but now finds that that method must be further modified in order to isolate the analogous bromine compound, on account of its greater instability toward heat.

Siegfried prepared only the acetic ester of this carbinol, using acetyl chloride as the acetylating agent. In the present study acetic anhydride has been used. Corrected melting points of the carbinol and its acetic ester as well as other new data concerning these compounds are also submitted.

In addition, the propionic, butyric and benzoic esters have been prepared and studied.

## Experimental Part

**Preparation of Tribromomethylphenylcarbinol.**—To a mixture of 37 g. of *freshly distilled* benzaldehyde and 130 g. of *dry* bromoform was added with constant stirring 4 g. of powdered potassium hydroxide over a half-hour period. The mixture was allowed to stand for two hours, ether was added and the resultant mixture filtered. The filtrate was distilled until the temperature reached 155° at 680 mm. It was then steam distilled to remove the remainder of the benzaldehyde and small amounts of benzoic acid. The residue was washed with dilute sodium bicarbonate solution, extracted with ether, dried over sodium sulfate and the ether distilled off. The liquid residue crystallized out in one to two days. These crystals were dried on a porous plate and recrystallized from 50% acetic acid. Small amounts of crude material can be recovered from the mother liquor by dilution. A yield of 16–18 g. of plate-like crystals melting at 72.5–73.0° was obtained.

*Anal.* Calcd. for $C_8H_7OBr_3$: Br, 66.81. Found: Br, 66.78.

This compound is only very slightly soluble in water but readily soluble in carbon bisulfide, ethyl alcohol, methyl alcohol, benzene, acetone, ether, chloroform and carbon tetrachloride.

## Preparation of the Esters

The acetate and propionate were prepared by heating the carbinol with the corresponding anhydrides at 130–135° for three hours. Both readily formed plate-like crystals on pouring the reaction mixture into water. The acetate was recrystallized from 50% alcohol and the propionate from 75% acetic acid; m. p. of acetate, 133°.

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[1] Siegfried, *Chem. Centr.*, **1**, 606 (1899).

[2] Jocitsch, *ibid.*, [5] 1, 1013 (1897).

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

*Anal.* Calcd. for $C_{10}H_9O_2Br_3$: Br, 59.81. Found: Br, 59.75.

The melting point of the propionate is 70.5°.

*Anal.* Calcd. for $C_{11}H_{11}O_2Br_3$: Br, 57.79. Found: Br, 57.85.

In the case of the butyrate the use of the anhydride did not give as satisfactory results as butyryl chloride, with which the carbinol was heated at 60–90° for three hours. Even after careful purification and distillation this ester does not solidify on standing for several weeks at room temperature. It is a thick viscous liquid of b. p. 205–207° at 220 mm., $d_{20}^{20}$ 1.779.

*Anal.* Calcd. for $C_{12}H_{13}O_2Br_3$: Br, 55.90. Found: Br, 55.85.

The benzoate was prepared by treatment with benzoyl chloride according to the usual procedure of the Schotten–Baumann reaction. On recrystallization from 95% alcohol clusters of needles are obtained. It melts at 146°.

*Anal.* Calcd. for $C_{15}H_{11}O_2Br_3$: Br, 51.81. Found: Br, 51.76.

The average yield of all of these esters was 85%.

All of the esters are insoluble in water and with the exception of the benzoate readily soluble in carbon disulfide, ethyl alcohol, methyl alcohol, benzene, acetone, ether, chloroform and carbon tetrachloride, the benzoate being much less readily soluble in ethyl and methyl alcohols than the others.

## Summary

Tribromomethylphenylcarbinol and its acetic, propionic, butyric and benzoic esters have been prepared and studied.

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# SYNTHESIS OF 1,4-PENTADIENE

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Among various series of unsaturated hydrocarbons the least explored field is that of the 1,4-dienes. According to Beilstein's "Handbook" only a few open-chain 1,4-dienes are known, *i. e.*, hexadiene-1,4, and 4-propylheptadiene-1,4. The first member of the series of diolefins with isolated double bonds has attracted the attention of many chemists. Several investigators have tried to prepare 1,4-pentadiene. Demjanov[2] and Demjanov and Dojarenko[3] on heating pentamethylenediamine nitrate or treating 1,5-di-iodopentane with alcoholic potash obtained among other products a small amount of a substance which on bromination yielded the tetrabromide of 1,4-pentadiene. Thiele[4] and others tried to prepare the hydrocarbon by exhaustive methylation of piperidine but

[1] Beilstein, "Handbuch org. Chem.," 1918, Bd. I, p. 253.

[2] Demjanov, *J. Russ. Phys.-Chem. Soc.*, **26**, 665 (1894).

[3] Demjanov and Dojarenko, *Ber.*, **40**, 2589 1908).

[4] Thiele, *Ann.*, **319**, 228 (1901).