[Contribution from the Research Laboratory of Parke, Davis & Co.]

# STUDIES ON DERIVATIVES OF TRIHALOGEN TERTIARY-BUTYL ALCOHOLS.

## II. THE PROPIONIC AND BUTYRIC ESTERS OF TRIBROMOTERTIARY-BUTYL ALCOHOL (BROMETONE).

By T. B. Aldrich.

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A continuation of my studies on derivatives of esters of trihalogen tertiary-butyl alcohols has led to the preparation of the propionic ester as well as the butyric ester of brometone. In several attempts to prepare these esters direct from the acids using zinc chloride as suggested by R. Wolffenstein, A. Loewey and M. Bachstez[1] in the preparation of chloretone esters, decomposition apparently took place without formation of the ester, unvariably giving rise to a volatile substance very irritating to the eyes. This method was therefore discarded and the ester prepared by allowing the acid chloride to act on the alcohol. As has been emphasized in one of my previous articles[2] on the subject of esters, it is desirable to dehydrate the halogen alcohol as much as practicable by allowing it to stand in a desiccator over calcium chloride (not sulfuric acid), thus economizing material.

The propionyl chloride, as well as the butyryl chloride, was prepared in the usual way by allowing phosphorus trichloride to act on the purified acid. The fraction of propionyl chloride boiling at 76 to 77.5° and that of butyryl chloride boiling at 99 to 100.5° (uncorr.) were employed in the preparation of the respective esters.

### Propionic Ester of Brometone.

Four parts of brometone were placed in a suitable flask and one part of the propionyl chloride added. Most of the brometone immediately dissolved, and hydrochloric acid gas was given off. The last portions of the gas were driven off by heating for some time on the steam bath. The contents of the flask were then shaken with 100 cc. of 10% sodium hydroxide, the mixture heated on the steam bath for a short time, thoroughly washed out with water and extracted with ether.[3] The yield in an impure form in one instance was 73% of the theoretical. Recrystallized from hot alcohol white crystals melting at 27° were obtained.

Bromine determinations (Carius) carried out with a product recrystallized several times from moderately strong alcohol gave the following results:

Subst., 0.2276, 0.1987, 0.2237 g. Bromine, 0.1492, 0.1288, 0.1466 g.
Calc. for $C_7H_{11}O_2Br_3$: Br, 65.39. Found: 65.55, 64.79, 65.53.

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[1] *Ber.*, 48, 2035 (1915).

[2] T. B. Aldrich and C. P. Beckwith, This Journal, 38, 2740 (1916).

[3] On adding *very cold* water during the process of washing the oil solidified completely; on warming to body temperature, however, it melted.

These results are sufficiently near the theoretical requirement to characterize the compound as the propionic ester without the necessity of a combustion analysis.

The ester is extremely soluble in strong alcohol, acetone, chloroform, ether, glacial acetic acid, benzene, etc., practically insoluble in water. It is precipitated as an oil from its alcoholic solution by water. The odor resembles that of the acetic esters very closely. Boiling with water or 10% sulfuric acid decomposes the ester slowly while boiling with 10% caustic soda decomposes it more rapidly. It is decomposed into the alcohol and acid very quickly by boiling a few minutes with an excess of conc. nitric acid, conducting itself in this respect toward hot nitric acid in the same way as do the acetic esters, since it is necessary only to cool after boiling and add water when the alcohol is thrown out in the form of a white solid. The compound volatilizes very slowly in the air, and is characterized similar to the other ester thus far studied, by its general stability.

R. Wolffenstein, A. Loewry and M. Bachstez[1] state briefly that the *propionic acid ester of chloretone* is a yellowish oil boiling at 88 to 90°, at 14 mm. It has not been determined exactly where the brometone ester boils but it has been shown with certainty that it boils higher than does the chloretone ester.

## Butyric Ester of Brometone.

In the preparation of this ester, as previously mentioned, butyryl chloride boiling at 99 to 100.5° was employed.

The preparation of the ester as well as its purification was carried out in general according to the method already described under the propionic ester.

After drying the ethereal extract over calcium chloride the ester was fractionated under reduced pressure and a fraction boiling fairly constant at 144 to 145° under 13 to 14 mm. pressure obtained.

Bromine determinations (Carius) carried out with this fraction gave the following results:

Subst., 0.2137, 0.2035 g. Bromine, 0.1351, 0.1291 g.

Calc. for $C_8H_{13}O_2Br_3$ : Br, 63.00. Found: 63.19, 63.44; average, 63.21.

This ester has approximately the same solubilities as the propionic ester and its odor resembles that of the other aliphatic ester in general but there is a faint suggestion of the presence of butyric acid. It conducts itself toward boiling water, sulfuric acid, alkali or conc. nitric acid the same as the propionic ester.

The compound is slightly volatile with steam; in the air it volatilized very slowly. It is apparently less volatile than either the acetic or propionic ester.

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[1] *Ber.*, 48, 2035 (1915).

The following preliminary data relative to the pharmacological tests were kindly furnished me by my associate, Mr. L. W. Rowe:

"Neither the butyric nor the propionic ester of brometone appears to possess anesthetic properties. The propionic ester is the more readily absorbed following hypodermic injection and is much less irritating than the butyric ester. Neither ester exerts a very appreciable action upon the heart or general circulation as the intravenous injection of a rather large dose of each into an anesthetized dog caused only a very slight fall in blood pressure. They are both comparatively inactive pharmacologically due to the probable fact that they are not decomposed into soluble constituents having a typical physiological action and are rather slowly absorbed. In this respect they are similar to other esters of this series."

DETROIT, MICHIGAN.

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# ORGANIC CHEMICAL REAGENTS. II.[1] AMYLENE, TERTIARY AMYL ALCOHOL.

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Amylene is a substance which is used at one time or another in most organic chemical laboratories either as a reagent or as a substance from which to prepare certain organic compounds such as tertiary amyl alcohol. In spite of its comparatively simple nature, it is in general considered not only an expensive substance but also one rather troublesome to prepare. For this reason we have studied the various methods for its production, and two which have proved satisfactory are described in detail below. One of these may be used if only small amounts, the other if large amounts of amylene are required.

Tertiary alcohols in general can be dehydrated with the production of unsaturated hydrocarbons far more readily than secondary or primary alcohols. Hence it is not surprising that oxalic acid serves as a convenient reagent for the preparation of trimethyl ethylene from tertiary amyl alcohol.[2] Tertiary amyl alcohol is, however, usually prepared from isoamylene and hence the reverse reaction becomes of less practical importance except as a method for the preparation of pure trimethyl ethylene from a mixture of isoamylenes.

Dehydration of primary alcohols for the preparation of alkylene hydrocarbons encounters increased difficulties as one goes higher in a given

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[1] This publication is the second in the series of those describing the results of the investigations at the University of Illinois on various organic chemical reagents. The first publication appeared in THIS JOURNAL, 40, 1281 (1918).

[2] *Friedlaender*, 3, 980; D. R. P. 66,866.