# [Contribution from the Research Department, the Edwal Laboratories]

## $\alpha$ -Methylallylamine

By John Krueger and Morton Schwarcz

Methods for the preparation of crotylamine  $(\gamma$ -methylallylamine)<sup>1</sup> and  $\beta$ -methylallylamine<sup>2</sup> have been known for some time. The remaining member of the series,  $\alpha$ -methylallylamine, which might be regarded as the allylic rearrangement product of crotylamine, has not been described.<sup>3</sup> We now report the isolation and characterization of  $\alpha$ -methylallylamine and a convenient method for its preparation from crotyl alcohol.

Charon<sup>4</sup> chlorinated crotyl alcohol and obtained a "crotyl chloride" boiling at 77°. The work of Winstein and Young<sup>5</sup> has shown this chloride to be most probably a mixture of crotyl chloride and of  $\alpha$ -methylallyl chloride (methylvinylcarbinyl chloride). Charon prepared a "crotyl mustard oil" from "crotyl chloride" which yielded a thiourea derivative of m. p. 105°. This so-called "crotyl mustard oil" was shown recently by Mumm and Richter<sup>6</sup> to consist chiefly of  $\alpha$ methylallyl isothiocyanate, for these authors were able to hydrogenate the thiourea derivative to a product identical with the thiourea derivative they prepared from *dl-s*-butyl isothiocyanate.

We have repeated Charon's work on the preparation of "crotyl mustard oil" and have observed the product boils unsharply at  $160-170^{\circ}$ . The oil we obtained, when treated with ammonia, furnished a thiourea derivative of m. p.  $106^{\circ}$ obviously identical with the compound described by Charon and by Mumm and Richter. In addition, we also isolated a compound of m. p.  $60^{\circ}$  in small amounts, which may be the thiourea derivative of crotyl isothiocyanate. We plan to investigate this substance more thoroughly when we obtain a larger amount of the material.

Acid hydrolysis of crude "crotyl mustard oil" yielded an amine which distilled at 60–72°. This crude amine, distilled through an efficient column, boiled at 62.3°. The b. p. of the amine so obtained did not change after several weeks of storage, and we believe the substance is a fairly stable compound.

Since crotylamine prepared by several different methods has been reported to boil above  $80^{\circ}$ ,<sup>1</sup> we considered our amine of b. p.  $62.3^{\circ}$  to be  $\alpha$ -methylallylamine. The possibility remained, however, that the amine might have been a geometrical isomer of crotylamine. We therefore hydrogenated the substance to *dl*-s-butylamine, thus proving the structure of the carbon skeleton to consist of a branched chain.

By application of the "mustard oil reaction" to  $\alpha$ -methylallylamine, a mustard oil of b. p. 160–170° was obtained. The crude mustard oil furnished a thiourea derivative of m. p. 106°, identical with the thiourea derivative prepared from Charon's "crotyl mustard oil."

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### **Experimental Part**

 $\alpha$ -Methylallylamine.—The mustard oil prepared by the method of Charon<sup>4</sup> boiled at 160-170° and gave a thiourea derivative of m. p. 105°. Three hundred grams of crude "crotyl mustard oil" was refluxed for forty hours with 1200 cc. of concentrated hydrochloric acid.7 The homogeneous solution was extracted thrice with ether and then was neutralized with 40% sodium hydroxide solution. The solution was steam distilled. The distillate was treated in an ice-salt-bath with solid sodium hydroxide. The oily layer was separated and dried with solid potassium hydroxide. The substance boiling at 58-73° weighed 66 g. (35% yield). The crude amine so obtained was distilled through an efficient column. The main fraction, weighing 44 g., distilled at 62.3°. No other homogeneous substance has vet been isolated. The first half of the main fraction showed  $n^{20}D$  1.4155, and the last half of this fraction showed  $n^{20}D$  1.4150. The amine appeared to be quite stable for, after standing for several weeks, a sample distilled from an ordinary distilling flask boiled completely at 62.2-62.8°. The crude picrate obtained by treating an ethanol solution of the distilled amine with picric acid melted at 156°. After several recrystallizations from ethanol the picrate was obtained as sheaves of large pale yellow needles of m. p. 156.5-158°.

Anal.<sup>8</sup> Calcd. for  $C_{10}H_{12}O_7N_4$ : C, 40.0; H, 4.0. Found: C, 40.5; H, 4.2.

A careful fractionation of the crude amine mixture was necessary as this amine fraction before distillation through

<sup>(1) (</sup>a) Schindler, Monatsh., 12, 416 (1891); (b) Bookman, Ber., 28, 3114 (1895); (c) Galand, Bull. soc. chim. Belg., 39, 529 (1938).

<sup>(2)</sup> Tamele, Ott, Marple and Hearne, Ind. Eng. Chem., 33, 115 (1941).
(3) Dimethyl-(α-methylallylamine) obtained from α-methyl-

trimethyleneimine is described in German Patent 247,144 issued to Bayer and Company.

<sup>(4)</sup> Charon, Ann. chim., [7] 17, 262 (1899).

<sup>(5)</sup> Winstein and Young, THIS JOURNAL, 58, 104 (1936).

<sup>(6)</sup> Mumm and Richter, Ber., 73B, 843 (1940).

<sup>(7)</sup> Cf. "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1938, Vol. 18.

<sup>(8)</sup> Microanalyses by Dr. T. S. Ma, The University of Chicago.

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the column yielded a picrate which could be purified only with large losses to melt at  $153-155^{\circ}$ .

dl-s-Butylamine.—Three grams of  $\alpha$ -methylallylamine and 0.2 g. of Adams catalyst in 20 cc. of ethanol absorbed 1125 cc. of hydrogen during ten minutes (calcd. for 1 mole, 1050 cc.). The catalyst was filtered off and picric acid was added to the filtrate. The solution was chilled in an icesalt-bath, thereby yielding 6.0 g. of yellow picrate of m. p. 129–130°. After two recrystallizations from ethanol the substance was obtained as large, flat, pale yellow needles of m. p. 129–130.5°.

Anal. Calcd. for  $C_{10}H_{24}N_7O_4$ : C, 39.7; H, 4.7. Found: C, 39.7; H, 4.7.

The picrate of m. p.  $130^{\circ}$  we prepared from dl-s-butylamine (b. p.  $62-64^{\circ}$ ), obtained from two different sources showed no depression in mixture melting point with our analyzed picrate. We believe, therefore, our picrate of m. p.  $130.5^{\circ}$  to be a pure substance and the m. p. of 139- $140^{\circ}$  quoted for the picrate of dl-s-butylamine by Heilbron<sup>9</sup> to be an error.

We also prepared a picrate of m. p. 147 ° from *n*-butylamine. This picrate mixed with the picrate of dl-s-butylamine of m. p. 130 ° melted at 111-122 °.

 $\alpha$ -Methylallyl Isothiocyanate from  $\alpha$ -Methylallylamine. -- $\alpha$ -Methylallylamine (22.0 g.) dissolved in ether was

(9) Heilbron, "Dictionary of Organic Compounds," Vol. I. The Oxford University Press, 1934, p. 215.

treated with 25 cc. of carbon disulfide. The precipitate which was filtered off weighed 27 g. and melted at 106°. Even on drying in a vacuum at room temperature the substance decomposed. Twenty-seven grams of freshly prepared dithiocarbamate derivative was dissolved in 500 cc. of water and the solution was treated with 20 g. of mercuric chloride in 500 cc. of water. The suspension was steam distilled and the distillate was extracted with ether. The ethereal solution when evaporated gave a residue weighing 3.5 g. (17%) which distilled from 158-173°. The substance then began to decompose and the distillation was stopped. The distillate weighing 2.0 g. was redistilled and the boiling range observed was 155-165°. The distillate treated with aqueous-alcoholic ammonia furnished a thiourea derivative of m. p. 105°, identical (m. p. and m.m.p.) with the thiourea derivative described by Charon. For analysis the substance crystallized from ethyl acetate as large glistening white hexagons of m. p. 106°.

Anal. Calcd. for  $C_{5}H_{10}N_{2}S$ : C, 46.1; H, 7.7. Found: C, 46.3; H, 7.6.

#### Summary

 $\alpha$ -Methylallylamine has been isolated and characterized. A convenient route to this compound from crotyl alcohol has been described.

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## Pinacolonylbarbituric Acids

## By S. M. MCELVAIN AND ROBERT F. TAYLOR

The substituents in the 5-position of those barbituric acids that are effective hypnotics are generally two alkyl groups or a combination of an alkyl and an alkylene group and the variations of the chain length and branching of these groups account for many of the pharmacological characteristics of the members of this important group of drugs. The present paper is concerned with the preparation of some barbituric acids that have as one of the 5-substituents a different type of group, *viz.*, the pinacolonyl group.

These compounds were prepared by the following sequence of reactions

$$(CH_{3})_{3}CCOCH_{3} + O = C(COOC_{2}H_{5})_{2} \longrightarrow OH$$

$$(CH_{3})_{3}CCOCH_{2}C(COOC_{2}H_{5})_{2} \xrightarrow{-H_{2}O}$$

$$I$$

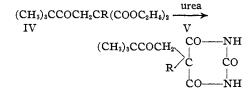
$$(CH_{3})_{3}CCOCH = C(COOC_{2}H_{5})_{2} \xrightarrow{H_{2} + Ni}$$

$$II$$

$$(CH_{3})_{3}CCOCH_{2}CH(COOC_{2}H_{5})_{2} \xrightarrow{RBr}$$

$$NaOC_{2}H_{5}$$

$$III$$



After a study of a wide variety of conditions it was found that pinacolone and oxomalonic ester reacted at  $160^{\circ}$  in eight hours to produce an 83%yield of the diethyl pinacolonyltartronate (I). This ester was surprisingly resistant to dehydration. Treatment with phosphorus pentoxide at 68°, or with iodine at 225°, left it practically unchanged. At higher temperatures the pentoxide produced some of the unsaturated ester II, but its formation was accompanied by considerable decomposition and charring. However, conversion of the ester I to the corresponding bromide with either phosphorus tribromide or anhydrous hydrogen bromide in benzene and the distillation of this bromide produced hydrogen bromide and the unsaturated ester II in 74-78%