

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, THE EDWAL LABORATORIES]

 α -Methylallylamine

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Methods for the preparation of crotylamine (γ -methylallylamine)¹ and β -methylallylamine² have been known for some time. The remaining member of the series, α -methylallylamine, which might be regarded as the allylic rearrangement product of crotylamine, has not been described.³ We now report the isolation and characterization of α -methylallylamine and a convenient method for its preparation from crotyl alcohol.

Charon⁴ chlorinated crotyl alcohol and obtained a "crotyl chloride" boiling at 77°. The work of Winstein and Young⁵ has shown this chloride to be most probably a mixture of crotyl chloride and of α -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 Richter⁶ to consist chiefly of α -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°. The oil we obtained, when treated with ammonia, furnished a thiourea derivative of m. p. 106° obviously identical with the compound described by Charon and by Mumm and Richter. In addition, we also isolated a compound of m. p. 60° 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 stor-

age, and we believe the substance is a fairly stable compound.

Since crotylamine prepared by several different methods has been reported to boil above 80°,¹ we considered our amine of b. p. 62.3° to be α -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 α -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

α -Methylallylamine.—The mustard oil prepared by the method of Charon⁴ 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 yet been isolated. The first half of the main fraction showed n_D^{20} 1.4155, and the last half of this fraction showed n_D^{20} 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.*⁸ Calcd. for C₁₀H₁₂O₇N₄: 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

(1) (a) Schindler, *Monatsh.*, **12**, 416 (1891); (b) Bookman, *Ber.*, **23**, 3114 (1895); (c) Galand, *Bull. soc. chim. Belg.*, **39**, 529 (1938).

(2) Tamele, Ott, Marple and Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941).

(3) Dimethyl-(α -methylallylamine) obtained from α -methyltrimethyleneimine is described in German Patent 247,144 issued to Bayer and Company.

(4) Charon, *Ann. chim.*, [7] **17**, 262 (1899).

(5) Winstein and Young, *This Journal*, **58**, 104 (1936).

(6) Mumm and Richter, *Ber.*, **73B**, 843 (1940).

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

(8) Microanalyses by Dr. T. S. Ma, The University of Chicago.

