

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF YALE UNIVERSITY]

The Synthesis of α -Naphthylacetic Acid

BY DEWITT T. KEACH

α -Allylnaphthalene is readily made by Tiffeneau and Daudel's¹ application of the Grignard reaction, yields of 70–75% being easily secured. It would appear from this and the work reported in this paper that in all cases where the aryl bromide is available, it should be possible to secure the substituted acetic acid, and an attempt to establish the generality of the reaction is being made.

α -Naphthylacetic acid was first prepared by P. Boessneck² in 1883 by heating together for several hours naphthoylformic acid, hydriodic acid and red phosphorus. Since that time it has been prepared by a number of investigators, (a) by the oxidation of α -naphthylacetaldehyde,³ (b) from α -methylnaphthalene through α -naphthylmethyl bromide and α -naphthylmethyl cyanide to the acid,⁴ (c) from α -naphthylacetaldehyde reacting with anhydrous sodium acetate, hippuric acid and acetic anhydride to form an azlactone, the acid being secured by the hydrolysis of this azlactone,⁵ (d) by the action of mono-haloacetic acid on naphthalene in the absence of free or combined alkali.⁶

It will be noticed from the information in the Experimental Part that the preparation of the acid by oxidation of α -allylnaphthalene depended on the establishment of satisfactory conditions.

The melting point given in the literature for this acid is 131°, while that found for the acid made by the oxidation method is 106°. Whatever the cause of this difference in melting point, it seems certain that the acid formed by the oxidation is α -naphthylacetic.

Experimental

Procedure.—Twenty grams of α -allylnaphthalene in 1200 cc. of 95% alcohol and 5 g. of sodium acetate in 50 cc. of water were placed in a five-liter flask, which was surrounded with an ice-salt bath. One hundred and fifty grams of potassium permanganate in 3.25 liters of water was then run into the flask slowly during constant stirring. When oxidation was complete, the manganese dioxide was filtered by suction and the solution concentrated to one-tenth its volume. While still alkaline the solution was extracted with ether, and concentrated hydrochloric acid added in excess to precipitate the crude α -naphthylacetic acid; 289 g. of α -allylnaphthalene gave a yield of crude acid dried *in vacuo* over calcium chloride and sodium hydroxide of 138 g., 43%. Repeated recrystallizations gave long colorless needles, m. p. 106°.

Anal. Ag salt 0.1823 g.: Ag, 0.0671 g. Molecular weight, 186.4.

- (1) Tiffeneau and Daudel, *Compt. rend.*, **147**, 678 (1908).
- (2) Boessneck, *Ber.*, **16**, 641 (1883).
- (3) Tiffeneau and Daudel, *Compt. rend.*, **147**, 679 (1908).
- (4) Mayer and Oppenheimer, *Ber.*, **49**, 2137, 2139 (1916).
- (5) Mauthner, *J. prakt. Chem.*, [2] **95**, 55–57 (1917).
- (6) Brit. Patent 330,918 (1929).

The methyl ester was prepared in the usual way, the yield being 86% of the theoretical. Hydrolysis of this ester gave an acid which after repeated recrystallization melted at 106°.

Identification of a By-Product.—The by-product obtained by extraction with ether while the reaction mixture was still alkaline appears on evaporation of the ether as a heavy brown oil which crystallizes on standing. Fourteen grams of this was obtained in the oxidation of 289 g. of α -allylnaphthalene. Recrystallized repeatedly from 30% alcohol it forms colorless prisms, m. p. 110°.

Anal. Subs., 0.2553 g.: H₂O, 0.1602 g.; CO₂, 0.7232 g.; H, 7.02; C, 77.25.

The simplest formula corresponding with this analysis is C₁₃H₁₄O₂ for which the calculated figures are H, 6.98, C, 77.20.

Anal. Calcd. for C₁₃H₁₄O₂: OH, 16.83. Found:⁷ OH, 16.43, 16.44.

The by-product is therefore α -naphthylmethylethylene glycol, C₁₀H₇CH₂CHOH-CH₂OH.

Summary

1. α -Naphthylacetic acid has been prepared in satisfactory yield by the oxidation of α -allylnaphthalene with potassium permanganate in alkaline solution.
2. A by-product during the oxidation has been shown to be α -naphthylmethylethylene glycol.

(7) Verley and Bolsing method, *Ber.*, **34**, 3354 (1901).
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RECEIVED FEBRUARY 24, 1933
PUBLISHED JULY 6, 1933

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Some Naphthyl Derivatives of Barbituric Acid

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In the quarter of a century since Fischer and Dilthey and Fischer and von Mering found that certain of the 5,5-disubstituted derivatives of barbituric acid could be used therapeutically as sedatives and hypnotics a large number of compounds of this type have been prepared. In 1930 the number of such compounds which had been made and tested was given as nearly a hundred¹ and many have been added since that time, but so far as the writer is aware none of those prepared to date contain the naphthyl group. There are two types of such compounds, those in which the naphthyl group is attached directly to the 5-carbon atom and those in which one or more methylene groups intervene between the 5-carbon atom and the naphthyl group. A study of both types is of considerable interest because of the properties of some of those containing the phenyl group, the naphthyl group having in many compounds an effect similar to that produced by the phenyl group.

In the work reported in this paper six barbituric acids which contain

(1) Shonle, Keltch and Swanson, *THIS JOURNAL*, **52**, 2449 (1930).