2. The latter has been synthesized from divinyl ether and found to be identical with Freundler's compound.

3. A new and simple synthesis of divinyl ether is described.

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EMPLOYMENT OF PYRIDINE AS CATALYST IN PRODUCTION OF DIMETHYL-ALPHA-NAPHTHYLAMINE

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Introduction

Subsequent experimentation carried on by the author with the view of ascertaining means of increasing the yield of terpineol from α-pinene and benzenesulfonic acid in acetic acid solution by inducing catalysis, developed the interesting fact that the presence of α-picoline ($NC_5H_4CH_3$) tended to increase the rate at which production occurred, accompanied by an increase in the actual yield of the product. This increase, however, is not greatly in excess of the quantity of terpineol obtained by the usual method.

It has been shown[1] that when an increase in the moisture content obtains the effect of such treatment upon the production of the substance sought is not proportional to the amount of water added at varying temperatures. It is believed that higher temperatures compensate for the decided increase in water content. The addition of α-picoline in minute and larger quantities increased the yields to an average of 2.35% in excess of those previously furnished. Unsuccessful attempts were made to enlarge this figure by the application of pyridine, (C_5H_5N), and related substances, but without avail.

It was considered advisable to test the effect of adding pyridine and certain of its homologs to reacting proportions of α-naphthylamine and methyl sulfate in alkaline solution to ascertain what effect, if any, the aromatic compound might have upon the mechanism of the reaction involved in the production of dimethyl-α-naphthylamine. The addition of α-picoline and that of the β-variety having been previously resorted to without the attainment of the sought-for objective, the contemplated step appeared feasible.

The discovery was made by the author that the yield of this methylated substitution product of naphthalene is greatly increased when the heterocyclic base is utilized as carrier. This compound has been used successfully as catalyst in Perkin's synthesis of cinnamic acid in this country[2] as well

[1] Germuth, *Am. J. Pharm.*, **99**, 402 (1927).

[2] Bacharach and Brogan, THIS JOURNAL, **50**, 3333 (1928).

as in Europe,[3] publication of the respective investigations occurring almost simultaneously. The results observed by the employment of pyridine in the role of catalyst in the production of dimethyl-α-naphthylamine form the theme considered and presented in this paper.

Method Employed.—Fourteen and three-tenth grams (0.1 mole) of α-naphthylamine was suspended in 25 cc. of water (temperature approximately 80°); to this was added 15 cc. of 40% sodium hydroxide and 25.3 g. (0.2 mole) of methyl sulfate. Each of these was added to the suspension of α-naphthylamine in water at equivalent rates, the temperature being maintained between 57 and 60°. The mixture was thoroughly stirred and the oil separated. Distillation *in vacuo* was then carried out. After this step was accomplished, about 25 g. of acetic anhydride was added. (A slight excess of the anhydride should be added until a constant temperature is maintained. The production of acetyl monomethyl-α-naphthylamine from monomethyl-α-naphthylamine present in solution is then attained.)

The mixture is poured into sufficient 28% sulfuric acid to provide for the presence of free hydrogen ions. The temperature of the acid should not be greater than 15°. This is then rendered slightly alkaline with a 28% solution of sodium hydroxide and thoroughly agitated. The separated oil is vacuum distilled. Dimethyl-α-naphthylamine passes over at 130–132° under a pressure of 8 mm. of mercury.

Purity of Materials.—The pyridine utilized in this work was of C. P. grade, possessing a boiling point of 116.5° and a specific gravity of 1.0035 at 0°. It was deemed unnecessary to attempt further purification.

The methyl sulfate employed possessed a boiling point of 188.5° and the specific gravity was 1.3278 at 20°. This compound was free from methyl sulfuric acid.

A very pure grade of α-naphthylamine was obtained by the action of sodamide upon naphthalene at a temperature of 215–220°. This substitution product possessed a specific gravity of 1.2230 at 24.8° and melted sharply at 50.2°.

The sodium hydroxide was further purified and upon analysis was found to contain but a trace of carbonate.

Experimental Work

Ten portions of dimethyl-α-naphthylamine were prepared, using the method given in this paper. Table I enumerates the results observed, showing the corresponding quantities of material produced in the treated samples.

TABLE I

YIELD OF DIMETHYL-α-NAPHTHYLAMINE OBTAINED (WITHOUT PYRIDINE)

Sample no.	1	2	3	4	5	6	7	8	9	10
Actual yield, g.	9.0	8.9	8.9	8.8	9.0	8.9	8.8	8.9	8.6	8.9
% of theoretical	52.1	51.4	51.4	50.8	52.1	51.4	50.8	51.4	49.7	51.4

Average, 51.3.

It will be observed that the differences existing in percentages of yields obtained are not in excess of those usually encountered in experimental work of this nature, particularly when small amounts of materials are utilized.

[3] Kalnin, *Helv. Chim. Acta*, **11**, 2416 (1928).

Ten additional samples were now prepared and treated precisely as those constituting the former series except that 0.1 g. of pyridine was added to the contents of each container before the addition of sodium hydroxide and methyl sulfate. The percentage yield of dimethyl-α-naphthylamine was so increased by this procedure that further experimentation, employing varying quantities of pyridine, was immediately undertaken. Continued investigation disclosed the fact that when four drops (approximately 0.2 cc.) of pyridine, equivalent to eighty drops or approximately 4 cc. of pyridine per mole of α-naphthylamine, was added to the mixture, most gratifying results were noted.

Table II shows the increased yield of dimethyl-α-naphthylamine produced by the application of pyridine to the test solutions.

TABLE II

YIELD OF DIMETHYL-α-NAPHTHYLAMINE OBTAINED

Addition of pyridine, 4 cc. per mole of α-naphthylamine

Sample no.	1	2	3	4	5	6	7	8	9	10
Actual yield, g.	11.4	11.3	11.4	11.5	11.3	11.5	11.3	11.5	11.3	11.5
% of theoretical	65.9	65.1	65.9	66.4	65.1	66.4	65.1	66.4	65.1	66.4

Average, 65.8.

In each instance the purity of the dimethyl-α-naphthylamine was determined by the usual tests (reaction, specific gravity and boiling point), and the high degree of purity of the product confirmed.

Summary

The employment of pyridine as catalytic agent in the production of dimethyl-α-naphthylamine from α-naphthylamine and methyl sulfate increases the yield of the compound from an average of 51.3% to 65.8%, when this base is utilized in the proportion of four cubic centimeters of pyridine per mole of α-naphthylamine.

Smaller quantities than that advocated do not furnish the yield attained by the amount of pyridine stipulated. Larger proportions fail to increase the quantity of dimethyl-α-naphthylamine obtained under the conditions maintained. The material produced in the presence of pyridine is of high quality.

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