upon dilution with water. (c) Amides of primary amines where the amino group is attached to a tertiary carbon atom yield an olefin, an acid and ammonia upon steam distillation with 10% sulfuric acid.[5]

Cyclohexanone probably goes to cyclohexenylcyclohexanone in the presence of aluminum chloride and the condensation of cyclohexenylcyclohexanone and a nitrile is similar to the reaction of cyclohexene with hydrogen cyanide in the presence of aluminum chloride to give a 30% yield of N-formylcyclohexylamine[6] and to the reaction of nitriles and tertiary olefins to give N-tertiary alkyl amides.[5]

Acknowledgment.—The assistance of Dr. J. R. Downing of the Chemical Department, E. I. du Pont de Nemours and Company, Inc., is gratefully acknowledged for the interpretation of the infrared data.

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(5) Ritter and Minieri, THIS JOURNAL, **70**, 4045 (1948).

(6) Wieland and Dorrer, *Ber.*, **63**, 404 (1930).

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Methyl *n*-Propyl Ketone and its Conversion to *n*-Propylpyridine

BY RAYMOND P. MARIELLA AND ROGER STANSFIELD

In agreement with earlier workers,[1-4] ethyl formate was found to condense with the methyl group of methyl *n*-propyl ketone in the presence of sodium. This was established by converting the product (I) into the pyridone (II) and subsequent degradation to *n*-propylpyridine.

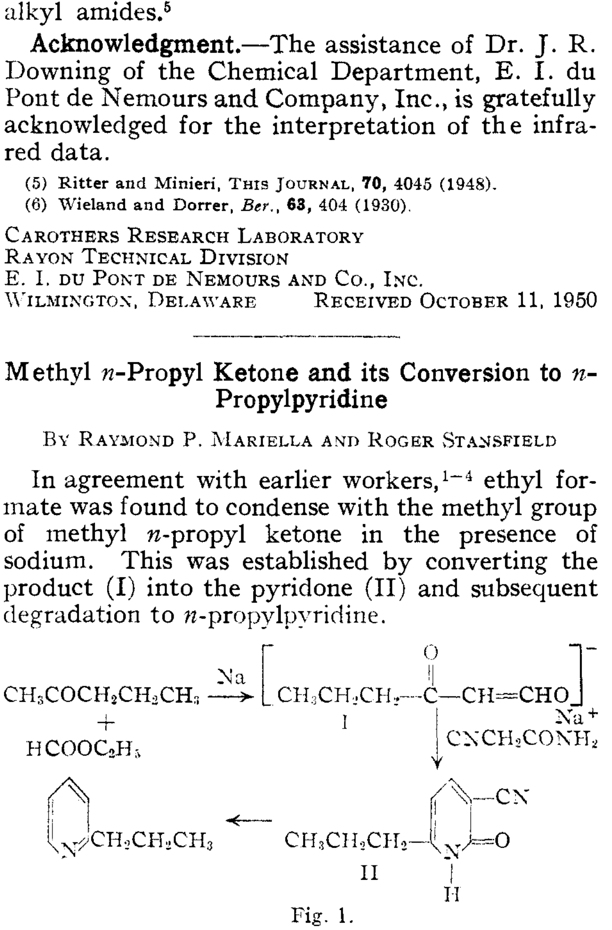

Fig. 1.

However, the condensation might have occurred partly at the methylene group, since the pyridone (II) could not be isolated in better than a 37% yield. The condensation product (I) was obtained in a 74% yield. These results are interesting because the previous workers had indicated that the methyl group was the only site of condensation. It was possible to isolate the free hydroxymethylene ketone as a colorless liquid, but in a poor yield (13%), as it decomposed rapidly.

Experimental[5]

Since the experimental details parallel those published before,[6] only the essential features will be mentioned.

3-Cyano-6-*n*-propyl-2(1)-pyridone (II).—From 46 g. of sodium metal ribbon in 1.5 l. of dry ether, by the addition of 172 g. of methyl *n*-propyl ketone (b.p. 101.3° at 752 mm.) and 148 g. of ethyl formate, there was obtained 200 g. (74% yield) of crude sodium salts as a yellow powder.

A solution of 136 g. of the above sodium salt and 90 g. of cyanoacetamide in 500 ml. of water, containing piperidine acetate catalyst, after refluxing for 3 hours, gave 100 g. of crude brown product.

A sample was recrystallized several times from absolute alcohol and resulted in white needles, m.p. 153°.

Anal. Calcd. for $C_9H_{10}N_2O$: C, 66.24; H, 6.18; N, 17.2. Found: C, 66.23; H, 6.41; N, 16.9.

The 100 g. obtained above represented very crude material since the m.p. was over a wide range, 120–145°. One recrystallization and treatment with Norit gave 60 g. (37% yield) of yellow prisms, m.p. 142–148°. An investigation of the mother liquor showed the presence of a dark-brown solid, softening in the range 50–110°, which appeared to be a complex mixture. Many attempts at purification using alcohol, acetone or glacial acetic acid as crystallizing solvents did not improve the melting point.

The Free Hydroxymethylene Ketone.—Fifteen grams of sodium salt was treated with excess sulfuric acid and shaken with ether. The ether was dried and removed *in vacuo*, leaving a dark-red liquid. Distillation gave 1.7 g. (13% yield) of colorless liquid, b.p. 51° at 16 mm., $n^{24}{}_D$ 1.4190 and $d^{24}{}_4$ 1.009. This liquid rapidly darkened.

6-*n*-Propyl-2(1)-pyridone-3-carboxylic Acid.—A solution of 50 g. of recrystallized cyanopyridone (II) in 500 ml. of concentrated hydrochloric acid was refluxed for 6 hours and gave 49 g. (88%) of the acid. A sample was recrystallized several times from water, colorless powder, m.p. 160°.

Anal. Calcd. for $C_9H_{11}NO_3$: N, 7.7. Found: N, 7.8.

6-*n*-Propyl-2-pyridol.—From 31 g. of pyridone acid, by heating at 335° for 15 minutes, there was obtained 21.5 g. (92%) of colorless long needles. Sublimation produced short needles, m.p. 88–89°.

Anal. Calcd. for $C_8H_{11}NO$: N, 10.2. Found: N, 10.4.

6-Chloro-2-*n*-propylpyridine.—From a solution of 20 g. of pyridol and 33 g. of phosphorus pentachloride in 25 ml. of phosphorus oxychloride, there was obtained 7 g. (33%) of a colorless liquid, b.p. 81.0–81.2° at 6 mm., $n^{20}{}_D$ 1.5164, $n^{25}{}_D$ 1.5135 and $d^{25}{}_{25}$ 1.073.

Anal. Calcd. for $C_8H_{10}ClN$: N, 9.0. Found: N, 8.6.

2-*n*-Propylpyridine.—From 6.5 g. of the chloropyridine, using palladium-on-charcoal in acid solution, there was obtained 6.0 g. (92%) of colorless needles of 2-*n*-propylpyridine hydrochloride. The free base had the following physical constants: b.p. 166–167° at 750 mm., $d^{25}{}_{25}$ 0.912, and $n^{20}{}_D$ 1.4925. The derivatives had the following melting points: picrate 74°, chloroplatinate 161–162° and chloroaurate, 77–80°, and did not depress the m.p. of authentic samples.[7]

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(1) L. Claisen and N. Stylos, *Ber.*, **21**, 1148 (1888).

(2) E. Benary, H. Meyer and K. Charisius, *ibid.*, **59**, 110 (1926).

(3) E. Benary, *ibid.*, **59**, 600 (1926).

(4) W. Gruber and H. Schlogl, *Monatsh.*, **81**, 83 (1950).

(5) Analyses by Misses Virginia Hobbs and Margaret Hines.

(6) R. P. Mariella, THIS JOURNAL, **69**, 2670 (1947).

(7) R. P. Mariella, L. Peterson and R. Ferris, *ibid.*, **70**, 1494 (1948).

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Quinoxaline Studies. II. The Preparation of 2-Hydroxy-3,6-dimethylquinoxaline and 2-Hydroxy-3,7-dimethylquinoxaline

BY BURTON MARKS[1] AND HARRY P. SCHULTZ

The condensation of 3,4-diaminotoluene with pyruvic acid was reported by Hinsberg[2] to produce a quinoxaline of undetermined structure melting at 220°. A low yield of another quinoxaline, m.p. 238°, presumably 2-hydroxy-3,7-dimethylquinoxa-

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(1) Abstracted in part from a thesis by Burton Marks, presented to the Graduate Faculty of the University of Miami, in partial fulfillment of the requirements for the degree of Master of Science in chemistry, August, 1950.

(2) O. Hinsberg, *Ann.*, **237**, 351 (1887).