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.

(5) Ritter and Minieri, THIS JOURNAL, **70**, 4045 (1948).
(6) Wieland and Dorrer, *Ber.*, **63**, 404 (1930).

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WILMINGTON, DELAWARE RECEIVED OCTOBER 11, 1950

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.

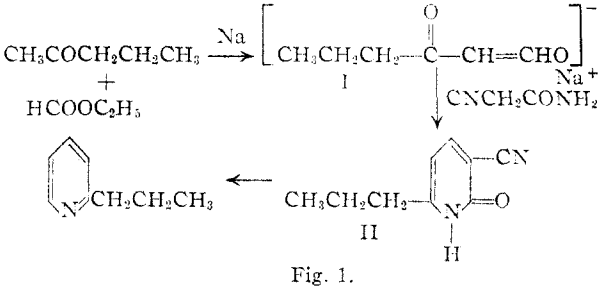

Fig. 1.

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.

(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).

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]

(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-

(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).

line, resulted from the condensation of 3,4-diaminotoluene with ethyl α-bromopropionate.[3]

We have prepared by unequivocal means both 2-hydroxy-3,6-dimethylquinoxaline and 2-hydroxy-3,7-dimethylquinoxaline. The former melts at 254–255°, and the latter at 243–244° (reported[4] 237°).

The material melting at 220° described by Hinsberg[2] appears to be an eutectic of the above two isomers. A melting point diagram of these two substances is given in Fig. 1.

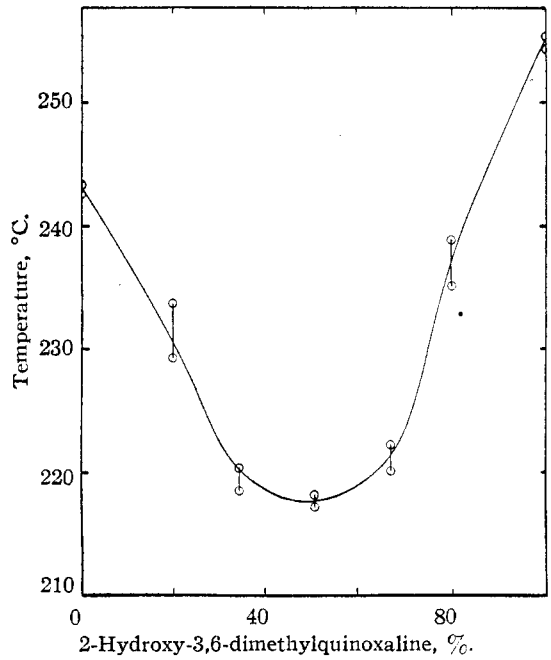

Fig. 1.—Melting point–composition curve of 2-hydroxy-3,6-dimethylquinoxaline and 2-hydroxy-3,7-dimethylquinoxaline; melting point range of each mixture indicated by O—O.

2-Hydroxy-3,6-dimethylquinoxaline was prepared from 3-nitro-4-acetamidotoluene. 3-Amino-4-acetamidotoluene was prepared by reduction of 3-nitro-4-acetamidotoluene over palladium-charcoal. Poor yields of the isolated 3-amino-4-acetamidotoluene resulted, due to cyclization of the amine to 2,6-dimethylbenzimidazole when the reduction solvent was removed. Hence, except for preliminary investigations, the reduced product was not isolated.

3-Amino-4-acetamidotoluene was condensed with ethyl α-bromopropionate to give the ethyl ester of N-(2-acetamido-5-methylphenyl)-*dl*-α-alanine. Hydrolysis and cyclization of this ester were completed in acid solution. The intermediate dihydroquinoxaline was oxidized in basic solution with hydrogen peroxide to 2-hydroxy-3,6-dimethylquinoxaline.

The synthesis of 2-hydroxy-3,7-dimethylquinoxaline was effected by a shorter procedure than that employed by Hinsberg.[4] The condensation of 3-nitro-4-aminotoluene with α-bromopropionic acid gave N-(2-nitro-4-methylphenyl)-*dl*-α-alanine. This product was reduced over palladium-charcoal to 2-hydroxy-3,7-dimethyldihydroquinoxaline. The dihydro compound was not isolated, but was air-oxidized to 2-hydroxy-3,7-dimethylquinoxaline.

A preparation was carried out using Hinsberg's procedure[2] wherein 3,4-diaminotoluene was treated with pyruvic acid. The Hinsberg product obtained in this Laboratory was a mixture of 2-hydroxy-3,6-dimethylquinoxaline and 2-hydroxy-3,7-dimethylquinoxaline melting at 214–215°. Eight recrystallizations of this product from ethanol gave a small yield of the slightly less soluble 2-hydroxy-3,7-dimethylquinoxaline.

Hinsberg's condensation[3] of 3,4-diaminotoluene with ethyl α-bromopropionate was repeated, but his numerous recrystallizations of the impure condensation product were avoided by utilizing methods of purification which restricted recrystallizations from organic solvents. Obvious enrichment of the mixed isomers mentioned in the preceding paragraph was thereby circumvented. The melting point (222–228°) and mixed melting points of this reaction product with each of the pure isomers indicated a mixture in which there was more 2-hydroxy-3,7-dimethylquinoxaline than 2-hydroxy-3,6-dimethylquinoxaline.

Experimental Procedures

Ethyl Ester of N-(2-Acetamido-5-methylphenyl)-*dl*-α-alanine.—Into 75 ml. of ethanol was placed 19.4 g. (0.1 mole) of 3-nitro-4-acetamidotoluene[5] and 1 g. of 5% palladium chloride on charcoal.[6] The theoretical quantity of hydrogen was absorbed at 30° and four atmospheres in 1 hour. The reduction solution containing 3-amino-4-acetamidotoluene[7] was filtered and 120 ml. of water and 9.23 g. (0.051 mole) of ethyl α-bromopropionate[8] were added. The reaction mixture was heated on a steam-bath for 5 hours, then poured into 500 ml. of water. After 12 hours at 5° a precipitate of 8.42 g. (63% yield) of gray powder was obtained, m.p. 124–126°. The material was recrystallized from ethanol–water with negligible loss to give the ethyl ester of N-(2-acetamido-5-methylphenyl)-*dl*-α-alanine, m.p. 126.8–127.1°.

Anal. Calcd. for $C_{14}H_{20}O_3N_2$: N, 10.6. Found: N, 10.5.

3-Amino-4-acetamidotoluene could be isolated in only 10% yield from the reduction solution of 3-nitro-4-acetamidotoluene; 2,6-dimethylbenzimidazole was obtained in great quantity. When the isolated amine was condensed with ethyl α-bromopropionate, a 74% yield of the ethyl ester of N-(2-acetamido-5-methylphenyl)-*dl*-α-alanine melting at 126.8–127.1° was obtained. Analysis and mixed melting point proved the identity of the material prepared by the two different procedures.

2-Hydroxy-3,6-dimethylquinoxaline.—A mixture of 8.42 g. (0.032 mole) of the ethyl ester of N-(2-acetamido-5-methylphenyl)-*dl*-α-alanine, 50 ml. of water and 50 ml. of concd. sulfuric acid was stirred on a steam-bath for 4 hours. After cooling and neutralizing the solution, the precipitate was filtered and heated on a steam-bath for 2 hours in a solution of 15 ml. of 8% sodium hydroxide mixed with 15 ml. of 3% hydrogen peroxide solution. Again the solution was cooled and brought to *p*H 4 to give 0.9 g. of yellow crystals, m.p. 245–249°. For analysis the material was sublimed at 150° (1 mm.), then recrystallized from ethanol–water to give 0.5 g. (9% yield) of white crystals, m.p. 254–255°. (All melting points of these quinoxalines were obtained by placing the capillary melting point tube in an aluminum block 5 to 7° below the melting point to avoid extensive sublimation of the material.)

Anal. Calcd. for $C_{10}H_{10}ON_2$: N, 16.1. Found: N, 16.0.

(3) O. Hinsberg, *Ann.*, **248**, 77 (1888).
(4) O. Hinsberg, *Ber.*, **25**, 2419 (1892).
(5) A. McGookin and S. R. Swift, *J. Soc. Chem. Ind.*, **58**, 152 (1939).
(6) R. Mozingo, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 78.
(7) G. T. Morgan and F. M. G. Micklethwait, *J. Chem. Soc.*, **103**, 1397 (1913).
(8) N. Zelinsky, *Ber.*, **20**, 2026 (1887).

N-(2-Nitro-4-methylphenyl)-*dl*-α-alanine.—A mixture of 7.6 g. (0.05 mole) of 3-nitro-4-aminotoluene[5] and 3.83 g. (0.021 mole) of α-bromopropionic acid[9] was heated for 8 hours on a steam-bath. The cooled melt was extracted with 20 ml. of 15% ammonium hydroxide. The ammonium hydroxide solution was treated with charcoal, then acidified with 10% hydrochloric acid to give 2.1 g. of red crystals, m.p. 142–144°. Repetition of the above purification gave 1.8 g. (38% yield) of N-(2-nitro-4-methylphenyl)-*dl*-α-alanine, m.p. 149.5–150°. Hinsberg[4] prepared this compound by a different process, reporting a melting point of 148°.

2-Hydroxy-3,7-dimethylquinoxaline.—A solution of 2.65 g. (0.012 mole) of N-(2-nitro-4-methylphenyl)-*dl*-α-alanine in 40 ml. of ethanol was reduced over palladium–charcoal at 30° and two atmospheres of hydrogen until the theoretical quantity of hydrogen had been absorbed. Catalyst and solvent were removed, and the tan residue was dissolved in 35 ml. of 10% sodium hydroxide solution and oxidized by drawing air through the solution for 18 hours at 70–80°. The solution was cooled and clarified by filtration; the filtrate was brought to *p*H 4 with acetic acid, precipitating 2-hydroxy-3,7-dimethylquinoxaline. The precipitate was sublimed at 150° (1 mm.) to give 0.9 g. (43% yield) of white sublimate, m.p. 240–241°. The material was crystallized from ethanol–water to constant melting point with no appreciable loss of product, m.p. 243–244°. The melting point previously reported[4] was 237°.

Anal. Calcd. for $C_{12}H_{10}N_2O$: N, 16.1. Found: N, 16.1.

Absorption Spectra.—The ultraviolet absorption spectra in Fig. 2 were obtained on a Beckman model DU quartz spectrophotometer. All curves were run on analytical material at concentrations of 10 mg./l. of solvent; width of quartz sample cell was 1.003 cm.

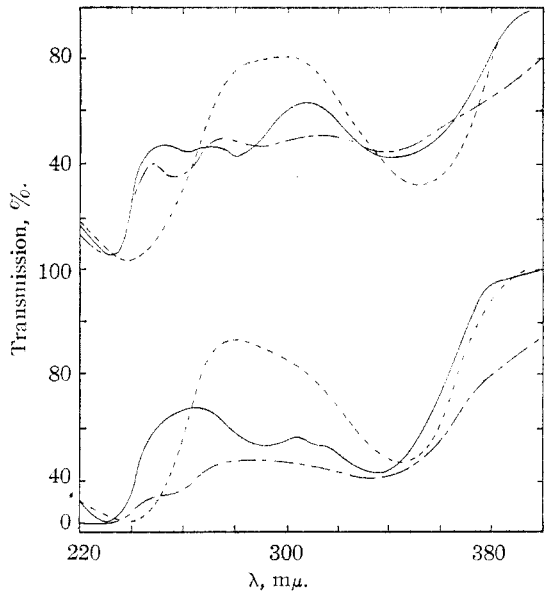

Fig. 2.—Ultraviolet absorption spectra of 2-hydroxy-3,6-dimethylquinoxaline, upper: 2-hydroxy-3,7-dimethylquinoxaline, lower; —, 95% ethanol; – – – – –, 0.1 *N* sodium hydroxide; — – — – 0.1 *N* hydrochloric acid.

(9) Eastman Kodak Company White Label material.

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CORAL GABLES, FLORIDA RECEIVED SEPTEMBER 19, 1950

The Preparation of N-Alkylethylenediamines

BY RUSSELL C. O'GEE AND HENRY M. WOODBURN[1]

N-Alkylethylenediamines are desirable intermediates for certain types of organic synthesis but their preparation has been unsatisfactory because of poor yields, complicated procedures, or methods limited to a specific type of substituent.

The situation has been reviewed by Aspinall[2] and by Coleman and Callen[3] both of whom proposed methods of their own. The first requires preliminary preparation of monoacetylethylenediamine and its N-benzenesulfonyl derivative and gives over-all yields of 10–33%. The second employs the catalytic addition of primary and secondary amines to ethylenimine, the reaction being favored by elevated temperatures. Actually, the only primary amines described are aniline and benzylamine.

The recent offering of 2-bromoethylamine hydrobromide in commercial quantities[4] suggested investigation of the reaction

$$RNH_2 + BrCH_2CH_2NH_2 \cdot HBr \longrightarrow RNHCH_2CH_2NH_2 + 2HBr$$

as a source of N-alkylethylenediamines. The reaction proved to be straightforward and easily carried out. Yields from both normal and branched-chain aliphatic primary amines are quite acceptable and the reaction has the double advantage of simplicity and the use of easily available reagents. Results of the investigation are summarized in Table I.

TABLE I

N-ALKYLETHYLENEDIAMINES ($RNHCH_2CH_2NH_2$)

R	Yield, %	B.p.,[a] observed °C.	Mm.	Ref.	Derivatives: Dihydrochloride m.p., °C. Obsd.	Ref.	Dipicrate m.p., °C. Obsd.	Ref.
CH_3	41	113–115	748	(2)	131	(5)	222–223	(5)
C_2H_5	40	125–127	743	(2)	168		193–194	(2)
n-C_3H_7	38	153–154	749	(6)	204–205		167–168[b]	(6)
i-C_3H_7	35	137–138	752	(7)	122–123		192–193	
n-C_4H_9	52	76–78	25	(6)	230	(5)	177	

[a] B.p.'s and m.p.'s uncorrected. [b] King and McMillan[6] report 224°. Our figure is supported by the following analysis: Calcd. for $C_5H_{14}N_2 \cdot 2C_6H_3N_3O_7$: C, 36.4; H, 3.6. Found: C, 36.6; H, 3.7.

Experimental

A solution of 102.5 g. (0.5 mole) of 2-bromoethylamine hydrobromide in 100 ml. of water was added to a 25% aqueous solution containing 2.5 moles of alkylamine. The resulting mixture was refluxed gently for 12 hours. It was then cooled and treated with solid sodium hydroxide until the base no longer dissolved. The solution separated into two layers as it became alkaline. The upper layer was taken off and the lower layer extracted with ether. The combined upper layer and extracts were dried over anhydrous potassium carbonate and fractionated through a 12″ column packed with glass helices.

The dihydrochlorides and dipicrates were made as an additional check on the identity of the diamines. The hydrochlorides not previously reported were analyzed for chlorine by the Mohr method. New picrates were analyzed for carbon and hydrogen by semi-micro carbon combustion technique.

N-Ethylethylenediamine dihydrochloride: Calcd. for $C_4H_{12}N_2 \cdot 2HCl$: Cl, 44.1. Found: Cl, 44.3.

N-Propylethylenediamine dihydrochloride: Calcd. for $C_5H_{14}N_2 \cdot 2HCl$: Cl, 40.6. Found: Cl, 40.7.

N-Isopropylethylenediamine dihydrochloride: Calcd. for $C_5H_{14}N_2 \cdot 2HCl$: Cl, 40.6. Found: Cl, 40.6.

(1) To whom inquiries regarding this article should be sent.

(2) Aspinall, THIS JOURNAL, **63**, 852 (1941).
(3) Coleman and Callen, *ibid.*, **68**, 2006 (1946).
(4) Dow Chemical Co., Midland, Michigan.
(5) Johnson and Bailey, THIS JOURNAL, **38**, 2135 (1916).
(6) King and McMillan, *ibid.*, **68**, 1774 (1946).
(7) Pearson, Jones and Cope, *ibid.*, **68**, 1225 (1946).