however, by extracting the crude crystals once with absolute ether in a Soxhlet apparatus. A mixed melting point with authentic vanillic acid[8] with the recorded m. p. 208–210°[8] was undepressed.

Veratric Acid and 4-Aminoveratrole.—The condensation of veratraldehyde 27.6 g., sodium azide 12.5 g. and concentrated sulfuric acid 118 ml. was essentially as described above but the time of hydrolysis was somewhat longer. Slightly discolored veratric acid, 25.4 g. or 84%, separated from the reaction mixture. One recrystallization from water and ethanol gave a pure product with the recorded[9] m. p. 179–181°. Extraction of the acid mother liquor with benzene gave less than 1 g. of oily crystals. The acidic solution was made strongly alkaline and extracted again with benzene. Evaporation of this extract and distillation of the residue under reduced pressure yielded 1.6 g. of colorless crystals that darkened in air. Their melting point of 87–88° agreed with that reported for 4-aminoveratrole.[10]

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(8) Misani and Bogert, *J. Org. Chem.*, **10**, 355 (1945).

(9) Goldschmiedt, *Monatsh.*, **6**, 379 (1885).

(10) Buck and Ide in "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 44.

DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY
McGILL UNIVERSITY
MONTREAL, CANADA
RECEIVED MARCH 9, 1948

[CONTRIBUTION FROM THE STEELE CHEMICAL LABORATORY OF DARTMOUTH COLLEGE, AND THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MICHIGAN]

8-Amino-2,4-Dimethylquinoline[1]

BY WYMAN R. VAUGHAN[2]

As a consequence of the tremendous recent interest in the derivatives of 8-aminoquinoline as antimalarial drugs it was found desirable to develop a satisfactory synthesis for 8-amino-2,4-dimethylquinoline. The present procedure was found to be a rapid and efficient method for the preparation of this substance, one of its advantages being that it obviates any extensive purification of the intermediate 8-nitro-2,4-dimethylquinoline.

Experimental

8-Nitro-2,4-dimethylquinoline.—One mole (157 g., 150 ml.) of 2,4-dimethylquinoline[3] was cooled to 0° and treated with 250 ml. of concentrated sulfuric acid which was added as rapidly as possible with good mechanical stirring. The resulting solution was then cooled to 0° and treated with a solution of 115 g. of potassium nitrate in 300 ml. of concentrated sulfuric acid with vigorous mechanical stirring, the temperature being maintained between 0 and 5° by means of an ice–salt-bath. When all of the nitrating solution had been added, the mixture was stirred for an additional fifteen minutes without cooling and then was poured onto 2500 g. of cracked ice. The resulting mixture was treated with 1500 ml. of concentrated ammonia and diluted to 6 l. with cold water, cooled to room temperature and filtered. The filter cake was placed in a 2-l. beaker with 1 l. of cold water and stirred vigorously until a uniformly fine suspension was obtained. It was then filtered with good suction, and the moist filter cake was recrystallized from 1 l. of 95% ethanol using norit and a heated funnel: yield 113–115 g. (51–67%), m. p. 115–125°.[4] This impure product is a mixture of 8-nitro-2,4-dimethylquinoline with one or more isomers. A second isomer, m. p. 109.6–110.1° cor., was isolated from the mother liquors from the recrystallization of the major product, but the structure of this substance has not as yet been determined.

Anal. Calcd. for $C_{11}H_{10}O_2N_2$: N, 13.86. Found: N, 14.0.

In view of the work of Price, Velzen and Guthrie[5] who isolated 6-nitro-2,4-dimethylquinoline, it would appear that this substance is either 5- or 7-nitro-2,4-dimethylquinoline, probably the former in view of the well-known resistance of the 7-position in quinoline toward nitration.[6]

8-Amino-2,4-dimethylquinoline.—A solution of 101 g. (0.5 mole) of 8-nitro-2,4-dimethylquinoline (m. p. 115–125°) in 375 ml. of concentrated hydrochloric acid was added from a dropping funnel to a well-stirred solution of 375 g. of stannous chloride dihydrate in 136 ml. of concentrated hydrochloric acid, the temperature being maintained at 40–50° by means of an ice-bath. Near the end of the reduction a yellow precipitate appeared. After complete addition of the nitro compound to the reducing solution there was added 2000 g. of cracked ice and a cooled solution of 850 g. of potassium hydroxide in 1 l. of water. The resulting mixture was vigorously stirred for 30 minutes and then filtered, and the residue was washed in the funnel with three portions of cold water totaling 1 l. The filter cake was pressed dry and then was dissolved in 1 l. of water containing 50 ml. of concentrated hydrochloric acid. In order to effect solution the mixture was boiled and then was treated at the boiling temperature with a liberal quantity of norit and filtered through a steam-heated funnel. Upon cooling there separated from the filtrate a mass of golden yellow needles, 71–87 g.[7] This product was dissolved in 500 ml. of boiling water, and the resulting solution was treated with 30 ml. of concentrated ammonia. The 8-amino-2,4-dimethylquinoline separated as an oil which solidified upon rapid cooling with continuous agitation. The mixture was allowed to stand for 30 minutes at room temperature, and then it was filtered: yield 51–61 g. (59–71%), m. p. 86–90°. If a very pure product is desired, the initial product may be recrystallized directly from 70–90° ligroin (10 ml. per g.) or converted to the hydrochloride, which is readily recrystallized from water. Highly purified 8-amino-2,4-dimethylquinoline is a colorless crystalline substance, m. p. 93.7–94.2° cor.[8]

Anal. Calcd. for $C_{11}H_{12}N_2$: N, 16.27. Found: N, 16.3, 16.23.

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(1) Part of the work described in this paper was done under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and Dartmouth College.

(2) Present address: Department of Chemistry, University of Michigan, Ann Arbor, Michigan.

(3) Vaughan, "Organic Syntheses," Vol. 28, in preparation; *cf.* Craig, THIS JOURNAL, **60**, 1458 (1938).

(4) Repeated recrystallization of a portion of this product from ethanol-water and finally from 95% ethanol yielded a very pure 8-nitro-2,4-dimethylquinoline, m. p. 147–147.5°. Price, Velzen and Guthrie give 149.5–150° cor., *cf.* ref. 5.

(5) Price, Velzen and Guthrie, *J. Org. Chem.*, **12**, 203 (1947).

(6) Bacharach, Haut and Caroline, *Rec. trav. chim.*, **52**, 413 (1933); *cf.* ref. 8.

(7) The hydrochloride thus obtained appears to be a dihydrate which loses some of its water of hydration upon standing in a dry atmosphere.

(8) Roberts and Turner, *J. Chem. Soc.*, 1856 (1927), give 89–92°.

ANN ARBOR, MICHIGAN
RECEIVED DECEMBER 23, 1947

Some 2,3-Dialkylpyridines and their Derivatives[1]

BY HENRY M. WOODBURN AND MAX HELLMANN

Our extension of Elderfield's work[2] on 2,3-dimethylpyridine to the synthesis of other 2,3-dialkylpyridines was interrupted by the war, and

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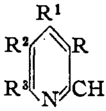
(1) From the M.A. thesis of Max Hellmann, University of Buffalo, June, 1947.

(2) Elderfield and Tracy, *J. Org. Chem.*, **6**, 54 (1941).

TABLE I

PROPERTIES OF 2-METHYL-3-ALKYLPYRIDINE DERIVATIVES



R	R¹	R²	R³	M. p., °C.	B. p.,[a] °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
n-C_3H_7	OH	CO_2Et	OH	192–193		$C_{12}H_{17}O_4N$	60.2	59.7	7.18	7.15
n-C_4H_9	OH	CO_2Et	OH	182–184		$C_{13}H_{19}O_4N$	61.6	61.9	7.57	7.41
n-C_3H_7	OH	H	OH	330–332 dec.		$C_9H_{13}O_2N$	64.6	64.5	7.84	7.73
n-C_4H_9	OH	H	OH	348–350 dec.		$C_{10}H_{15}O_2N$	66.3	66.0	8.34	8.38
n-C_3H_7	Cl	H	Cl		259	$C_9H_{11}Cl_2N$	Cl 34.7	34.6		
n-C_4H_9	Cl	H	Cl		275	$C_{10}H_{13}Cl_2N$	Cl 32.5	32.1		
n-C_3H_7	H	H	H	130–131[b]	200–201	$C_{15}H_{16}N_4O_7$[c]	49.5	49.8	4.44	4.46
n-C_4H_9	H	H	H	124–125[b]	222–223	$C_{16}H_{18}N_4O_7$[c]	50.8	50.5	4.80	4.92

[a] Corrected. [b] M. p. of the picrate. [c] Formula and analysis of the picrate.

shortly after its resumption the appearance of an abstract of a paper by Wibaut and Kooyman[3] made it inadvisable to proceed further along those lines. The applicability of the reaction scheme having been proved, we wish to report the synthesis and properties of 2-methyl-3-n-propylpyridine and of 2-methyl-3-n-butylpyridine together with those of certain intermediates used in their preparation.

Ethyl α-n-butyl β-aminocrotonate, for which no literature reference was found, was prepared from ethyl α-n-butylacetoacetate, ammonia and ammonium nitrate. It had a melting point of 41–42° and a boiling point of 116–118° (10 mm.).

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[3] Wibaut and Kooyman, *Rec. Trav. Chim.*, **63**, 231 (1944); *C. A.*, **41**, 450a (1947).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF BUFFALO
BUFFALO, NEW YORK

RECEIVED FEBRUARY 26, 1948

Products of the Interaction of Potassium Dihydrogenphosphide and n-Heptyl Bromide in Liquid Ammonia

BY GEORGE W. WATT AND R. C. THOMPSON, JR.

Alkali and alkaline earth metal dihydrogenphosphides prepared by the reaction between phosphine and solutions of these metals in liquid ammonia[1,2] continue to find application in the synthesis of derivatives of phosphine.[3]

Several years ago we studied several reactions of potassium dihydrogenphosphide in liquid ammonia and since further work is not anticipated it seems worth while to report the synthesis of n-heptylphosphine and its conversion to a product believed to be n-heptyl-phosphonous acid.

Phosphine was prepared by the action of sodium hydroxide solution on phosphonium iodide and dried over potassium hydroxide pellets. The dry gas was led into a solution of 2.7 g. of potassium in approximately 100 ml. of anhydrous liquid ammonia (contained in a flask provided with a stirrer and reflux condenser) until the characteristic blue color of the potassium solution was discharged. All reactants were protected from contact with the atmosphere. n-Heptyl bromide (11.9 g.) was added to the resulting pale yellow solution of potassium dihydrogen phosphide and the reaction mixture was stirred for two hours at −33.5°. The ammonia was evaporated and the residual liquid was removed in an atmosphere of carbon dioxide, extracted with 2 N hydrochloric acid solution, and the acid-insoluble fraction was distilled in an atmosphere of carbon dioxide to provide 6 ml. of a clear liquid, b. p., 73–74° at 30 mm. Boiling point determinations using capillary tubes gave consistently a value of 169.5°. This is a reasonable value for the boiling point of the anticipated n-heptylphosphine[4] which was apparently the primary reaction product. Despite precautions taken to avoid atmospheric oxidation while handling samples for analysis, this product was oxidized to a substance having an analytical composition corresponding to n-heptylphosphonous acid.

Anal. Calcd. for $C_7H_{17}PO_2$: C, 51.19; H, 10.44; P, 18.89. Found: C, 50.91; H, 10.48; P, 19.10.

This substance gave a negative test for halogen, exploded upon contact with fuming nitric acid, and was soluble in glacial acetic acid. Upon exposure to the atmosphere for several hours, it was further oxidized to a viscous liquid that boiled above 225°.

With potassium dihydrogenphosphide in liquid ammonia at −33.5°, bromo and iodobenzene react slowly, and ammonium chloroacetate reacts more rapidly to form products that have not been identified.

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[1] Joannis, *Compt. rend.*, **119**, 557 (1894); *Ann. chim. phys.*, [8] **7**, 101 (1906).

[2] Legoux, *Compt. rend.*, **207**, 634 (1938); **209**, 47 (1939); *Bull. soc. chim.*, [5] **7**, 545 (1940); *Ann. chim.*, **17**, 100 (1942).

[3] Knunyants and Sterlin, *Compt. rend. acad. sci. U. R. S. S.*, **56**, 49 (1947).

[4] For n-octylphosphine, Möslinger [*Ann.*, **185**, 65 (1877)] has reported b. p., 184–187°.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF TEXAS
AUSTIN 12, TEXAS

RECEIVED FEBRUARY 24, 1948

Reduction Products of m-Nitrostyrene

BY RICHARD H. WILEY AND NEWTON R. SMITH

The reduction of m-nitrostyrene to 3,3′-divinylazobenzene and to 2,2′-divinylbenzidine has been reported by Komppa.[1] These and two additional products, 3,3′-divinylazoxybenzene and 3,3′-divinylhydrazobenzene have been prepared in this study. Analytical data for these compounds are collected in Table I. The customary reagents were used for the transformations as described in

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[1] Komppa, Inaugural Dissertation, Helsingfors, *Ber.*, **26**, Ref. 677 (1893).