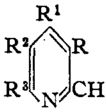
TABLE I

PROPERTIES OF 2-METHYL-3-ALKYLPYRIDINE DERIVATIVES



							Analyses, %			
							Carbon		Hydrogen	
R	R¹	R²	R³	M. p., °C.	B. p.,[a] °C.	Formula	Calcd.	Found	Calcd.	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.).

---

(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.

---

(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

---

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