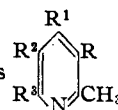


TABLE I

PROPERTIES OF 2-METHYL-3-ALKYLPYRIDINE DERIVATIVES



R	R ¹	R ²	R ³	M. p., °C.	B. p., ^a °C.	Formula	Analyses, %			
							Carbon		Hydrogen	
						Calcd.	Found	Calcd.	Found	
<i>n</i> -C ₃ H ₇	OH	CO ₂ Et	OH	192-193		C ₁₂ H ₁₇ O ₄ N	60.2	59.7	7.18	7.15
<i>n</i> -C ₄ H ₉	OH	CO ₂ Et	OH	182-184		C ₁₃ H ₁₉ O ₄ N	61.6	61.9	7.57	7.41
<i>n</i> -C ₃ H ₇	OH	H	OH	330-332 dec.		C ₉ H ₁₃ O ₂ N	64.6	64.5	7.84	7.73
<i>n</i> -C ₄ H ₉	OH	H	OH	348-350 dec.		C ₁₀ H ₁₅ O ₂ N	66.3	66.0	8.34	8.38
<i>n</i> -C ₃ H ₇	Cl	H	Cl		259	C ₉ H ₁₁ Cl ₂ N	Cl 34.7	34.6		
<i>n</i> -C ₄ H ₉	Cl	H	Cl		275	C ₁₀ H ₁₃ Cl ₂ N	Cl 32.5	32.1		
<i>n</i> -C ₃ H ₇	H	H	H	130-131 ^b	200-201	C ₁₅ H ₁₆ N ₄ O ₇ ^c	49.5	49.8	4.44	4.46
<i>n</i> -C ₄ H ₉	H	H	H	124-125 ^b	222-223	C ₁₆ H ₁₈ N ₄ O 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 Kooyman³ 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 con-

vided 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*-heptylphosphine⁴ 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 C₇H₁₇PO₂: 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.

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

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF TEXAS
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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).

(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) Kaunyants and Sterlin, *Compt. rend. acad. sci. U. R. S. S.*, **56**, 49 (1947).

TABLE I
 REDUCTION PRODUCTS OF *m*-NITROSTYRENE

Compound	Yield, %	Color	M. p., °C., cor.	Empirical formula	Carbon		Analyses, % Hydrogen		Nitrogen	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
3,3'-Divinylazoxybenzene	78	Yellow	39.5-41	C ₁₆ H ₁₄ N ₂ O	76.78	76.81	5.64	5.65	11.20	11.30
3,3'-Divinylazobenzene	81.5	Orange	84	C ₁₆ H ₁₄ N ₂	82.02	82.21	6.02	6.16	11.96	11.87
3,3'-Divinylhydrazobenzene	74.5	Faint yellow	96.5-97	C ₁₆ H ₁₆ N ₂	81.32	81.14	6.81	6.92	11.86	11.87
2,2'-Divinylbenzidine	30	White	123	C ₁₆ H ₁₆ N ₂	81.32	81.06	6.81	6.92	11.86	12.10
3-Aminostyrene hydrochloride polymer	84	Brown	Dec.	C ₈ H ₁₀ NCl	9.00	9.17

the experimental part. The azoxy compound was formed with zinc and ammonium chloride instead of the hydroxylamine usually obtained with this reagent. Polymeric products were obtained in the reduction of nitro to amino with zinc and hydrochloric acid; of nitro to azo with stannous chloride; of azoxy to azo with iron filings; and of azo to hydrazo with zinc and alcoholic sodium hydroxide. The azoxy compound polymerized on heating with benzoyl peroxide and the benzidine and azo compounds on heating without catalyst. The hydrazo compound decomposed on heating with benzoyl peroxide apparently without polymerization.

Experimental

Yields, physical properties, and analyses for the following products are listed in Table I.

m-Nitrostyrene was prepared by the decarboxylation of *m*-nitrocinnamic acid by a procedure similar to that previously attempted.³ A mixture of 20 g. of *m*-nitrocinnamic acid (E. K. Co.), 75 ml. of quinoline, and 3 g. of copper powder were heated at 185-190° so as to produce a steady evolution of carbon dioxide. After one and one-half hours of heating the mixture was acidified with 50% excess 3 *N* hydrochloric acid and steam distilled. The distillate was extracted with chloroform and the combined extracts were dried over anhydrous sodium sulfate. After distilling off the chloroform, the residue was fractionated from a modified Claisen flask to give 9.3 g., 60% of the theoretical amount, of *m*-nitrostyrene, b. p. 90-96° (3.5 mm.), *n*_D²⁰ 1.5836. Refractionation through a partial take-off column, 0.75 × 8 in. packed with Fenske rings gave a center cut, b. p. 96° (3.5 mm.), *n*_D²⁰ 1.5830. With larger quantities longer reaction times were required and lower yields were obtained than in the above experiment.

3,3'-Divinylazoxybenzene was prepared by the reduction of *m*-nitrostyrene with sodium methoxide in methanol⁸ or by reduction with zinc and ammonium chloride in aqueous ethanol.⁴ Heating the fused solid at 80° with 0.5% benzoyl peroxide gave an insoluble, infusible polymer.

3,3'-Divinylazobenzene.—To 0.68 g. of 3,3'-divinylhydrazobenzene in 75 ml. of ethanol was added 10 g. of ferric chloride hexahydrate in 25 ml. of hot water. After fifteen minutes water was slowly added to precipitate the azo compound, which was twice recrystallized from alcohol-water. Oxidation with sodium hypobromite or air in alcoholic sodium hydroxide also converted the hydrazo to the azo compound. Attempts to convert the azoxy to the azo compound by heating with iron filings gave polymeric products. The sample analyzed melted at 84° (cor.); Komppa¹ reported a m. p. of 38°. Heating at 110° for twenty-four hours gave an insoluble polymer which decomposed before melting when heated.

(2) Walling and Wolfstirn, *This Journal*, **69**, 852 (1947).

(3) Sudborough and James, "Practical Organic Chemistry,"

D. Van Nostrand and Company, New York, N. Y., 1934, p. 252.

(4) Sudborough and James, *ibid.*, p. 253.

3,3'-Divinylhydrazobenzene was prepared by zinc and alcoholic sodium hydroxide reduction⁸ of *m*-nitrostyrene. Attempts to reduce the azo to hydrazo compound with zinc and alcoholic sodium hydroxide gave only a polymer. On heating a mixture of solid the hydrazo compound and 0.5% benzoyl peroxide to 110° decomposition without apparent polymerization occurred.

2,2'-Divinylbenzidine was prepared in 30% yield by treating 3,3'-divinylhydrazobenzene with concd. hydrochloric acid in ether,⁸ m. p. 123° (cor.); reported¹ m. p. 124°. Heating to 135° converted the benzidine to an infusible, insoluble polymer.

m-Aminostyrene Polymer.—Reduction of *m*-nitrostyrene with zinc and hydrochloric acid gave a polymer which was precipitated as the hydrochloride on addition of excess hydrochloric acid to its aqueous acid solution.

(5) Gattermann-Wieland, "Laboratory Methods of Organic Chemistry," The Macmillan Company, New York, N. Y., 1932, p. 174.

(6) Gattermann-Wieland, *ibid.*, p. 176.

VENABLE CHEMICAL LABORATORY
UNIVERSITY OF NORTH CAROLINA

CHAPEL HILL, N. C.

RECEIVED MARCH 13, 1948

p-Alkoxybenzyl Grignard Reagents

BY M. G. VAN CAMPEN, DONALD F. MEISNER¹ AND
STANLEY M. PARMETER²

The alkoxybenzylmagnesium halides are valuable intermediates in the synthesis of stilbene derivatives particularly in the study of synthetic estrogenic agents. However, the general impression exists that these Grignard reagents cannot be prepared. This impression is probably due to the fact that in attempts to form the Grignard from such halides as *p*-methoxybenzyl chloride by the usual procedure, a nearly quantitative yield of the *p,p'*-dialkoxybibenzyl is obtained. By using a modification of the method reported by Gilman³ for the preparation of allyl Grignard reagents, it is possible to prepare *p*-alkoxybenzylmagnesium chlorides in acceptable yields. This is accomplished primarily by the use of a large excess of magnesium powder and slow addition of a dilute ether solution of the benzyl halide to the magnesium. Using the following general procedure 90% yields of *p*-methoxybenzylmagnesium chloride and *p*-benzyloxybenzylmagnesium chloride are consistently obtained.

Procedure.—A mixture of 2 to 2.5 g. atoms of magnesium turnings and 2 to 2.5 g. atoms of magnesium

(1) Present address: C. J. Patterson Co., Kansas City 2, Missouri.

(2) Present address: Eastman Kodak Research Laboratories, Rochester, New York.

(3) Gilman and McClumphy, *Bull. soc. chim.*, [4] **43**, 1322 (1926).