Table I

Ultraviolet Absorption

	$\lambda_{max.}$, mμ	$\epsilon_{max.} \times 10^{-3}$	Solvent
Pyridine	246	1.84	CH_3OH
	251	2.45	
	257	2.71	
	263	1.84	
2-Methyl-5-Ethyl-pyridine	268	3.63	C_2H_5OH
	275	2.75	
Pyridine oxide	213	16.7	C_2H_5OH
	265	12.9	
4-Methylpyridine oxide	212	17.2	C_2H_5OH
	266	14.7	
5-Ethyl-2-pyridylmethyl acetate	262		
	265	4.77	C_2H_5OH
	271		
5-Ethyl-2-pyridylmethanol	263		
	267	3.64	C_2H_5OH
	273		
1-(2-Pyridyl)-ethanol	256		
	262	3.27	C_2H_5OH
	267		
2-Pyridol[a]	227	10	
	297	6.32	C_2H_5OH

[a] H. Specker and H. Gawrosch, *Ber.*, **75B**, 1338 (1942).

The reaction has been demonstrated for 2-methyl-, 4-methyl-, 5-ethyl-2-methyl- and 2-ethylpyridine oxides. In the latter case rearrangement takes place to yield 1-(2-pyridyl)-ethyl acetate rather than 2-(2-pyridyl)-ethyl acetate.

The reaction of quinaldine oxide with benzoyl chloride and sodium hydroxide, originally investigated by Henze[1] has recently been discussed by Pachter,[2] who concluded that the product was 2-quinolinemethyl benzoate. Pachter's interpretation of Henze's reaction is in accord with the results reported here.

Experimental

Pyridine N-Oxides.—The oxides were prepared by reaction of the appropriate pyridine with hydrogen peroxide in acetic acid using a procedure substantially identical with that described by Ochiai.[3] Pyridine oxide had b.p. 122–124° (5 mm.), m.p. 66° (lit.[4] 66–68°), and n^{26}D 1.6118 (taken on the supercooled liquid); 2-methylpyridine oxide, b.p. 123° (9 mm.) and n^{25}D 1.5854; 2-ethylpyridine oxide, b.p. 109–113° (4 mm.), n^{25}D 1.5707; 2-methyl-5-ethylpyridine oxide, b.p. 147° (11 mm.), and n^{26}D 1.5634.

4-Methylpyridine oxide had m.p. 186–188° after recrystallization from ethanol/ethyl acetate. Ultraviolet absorption confirmed its structure.

Anal. Calcd. for C_6H_7ON: C, 66.04; H, 6.46; N, 12.83. Found: C, 65.59; H, 6.55; N, 12.54.

5-Ethyl-2-pyridylmethyl Acetate.[5]—Acetic anhydride (125 ml.) was stirred at 60–65° while 34 g. of 5-ethyl-2-methylpyridine oxide was added dropwise in about 10 min. The temperature of the red solution was held at 60–65° for 1.5 hr., first by the use of an ice-bath and later by gentle heating. Acetic anhydride was removed by distillation and the residue fractionated to yield a main fraction (26.8 g.) which had b.p. 120–127° (5 mm.), n^{25}D 1.5005.

Anal. Calcd. for $C_{10}H_{13}O_2N$: C, 67.01; H, 7.31; N, 7.82. Found: C, 67.56; H, 7.38; N, 8.33.

Infrared absorption of this compound indicated the presence of an aromatic nucleus (6.2–6.3 μ) and an ester group (C=O, 5.8 μ; C–O–C, 8.1 μ). Ultraviolet absorption confirmed the presence of an aromatic nucleus and ruled out the possibility of a pyridine oxide or a pyridone (see Table I).

5-Ethyl-2-pyridylmethanol.—An 8.0-g. sample of 5-ethyl-2-pyridylmethyl acetate was saponified by heating under reflux with 50 ml. of 10% sodium hydroxide. The alcohol was separated by extraction with methylene chloride. The dried methylene chloride solution was distilled to give 4.6 g. of colorless 5-ethyl-2-pyridylmethanol, b.p. 116–117.5° (5 mm.), n^{25}D 1.5299.

Anal. Calcd. for $C_8H_{11}ON$: C, 70.04; H, 8.08; N, 10.22. Found: C, 70.00; H, 8.29; N, 11.06.

Infrared absorption of this compound indicated the presence of an aromatic nucleus (6.2–6.3 μ) and a primary hydroxyl group (3.1 and 9.3–9.5 μ). Ultraviolet absorption confirmed the presence of an aromatic nucleus and ruled out the possibility of a pyridine oxide or a pyridone (Table I).

2-Pyridylmethanol.—2-Methylpyridine oxide was rearranged in acetic anhydride essentially as described above. The crude 2-pyridylmethyl acetate, b.p. 112–117° (5 mm.), was saponified with sodium hydroxide to give 2-pyridylmethanol, b.p. 111–112° (15 mm.) (lit.[6] 112° (16 mm.)). The picrate was prepared in the usual way and recrystallized several times from ethanol, m.p. 159–161° (lit.[6] 159°).

1-(2-Pyridyl)-ethanol.—A sample of 2-ethylpyridine oxide was rearranged in a similar way to give 1-(2-pyridyl)-ethyl acetate, b.p. 89–93° (3 mm.), n^{25}D 1.4913, yield 66%.

The ester was saponified to give a 60% yield of 1-(2-pyridyl)-ethanol, b.p. 85–89° (5 mm.), and n^{25}D 1.5253. Infrared absorption of this compound indicated the presence of an aromatic nucleus (6.2–6.3 μ) and a secondary hydroxyl group (3.1 and 9.0–9.3 μ).

A chloroplatinate was prepared in the usual way, m.p. 169–172° dec.

Anal. Calcd. for $(C_7H_9NO)_2 \cdot H_2PtCl_6$: Pt, 29.8. Found: Pt, 29.88.

It will be noted that the physical constants observed for our 1-(2-pyridyl)-ethanol are quite different from those reported for the solid of indefinite melting point obtained by Pinner[7] and called 1-(2-pyridyl)-ethanol by him. It appears highly likely that Pinner actually had the corresponding pinacol, a possibility which he recognized.

The same alcohol was isolated from a similar reaction in which the acetic anhydride was replaced by propionic anhydride.

4-Pyridylmethyl Acetate—Treatment of 33.5 g. of methylpyridine oxide with acetic anhydride following the procedure outlined above yielded 24 g. of a liquid, b.p. 85–95° (4 mm.). This material was presumed to be 4-pyridylmethyl acetate, but a conclusive identification was not made.

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(1) M. Henze, *Ber.*, **69**, 534 (1936).

(2) I. J. Pachter, This Journal, **75**, 3026 (1953).

(3) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

(4) J. Meisenheimer, *Ber.*, **59**, 1848 (1926).

(5) O. H. Bullitt, Jr., U. S. Patent 2,663,711 (Dec. 22, 1953).

(6) C. D. Harries and G. H. Lenart, *Ann.*, **410**, 107 (1915).

(7) A. Pinner, *Ber.*, **34**, 4241 (1901); *Beilstein*, **21**, 50 (1910).

1,2-Di-(2-pyridyl)-ethane[1,2]

By Paul G. Campbell and Peyton C. Teague

Received November 16, 1953

Edwards and Teague[3] obtained a compound $C_{12}H_{12}N_2$ as a by-product of the preparation of 2-pyridylmethanol by the air oxidation of 2-picolyllithium. This compound was not identified but was assumed to be 1,2-di-(2-pyridyl)-ethane. Thayer[4] later prepared the same compound by heating 2-picoline with sulfur.

In order to confirm the structure and to obtain the compound in good yield, a study was made of

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(1) This work was supported in part by a Frederick Gardner Cottrell Grant from the Research Corporation.

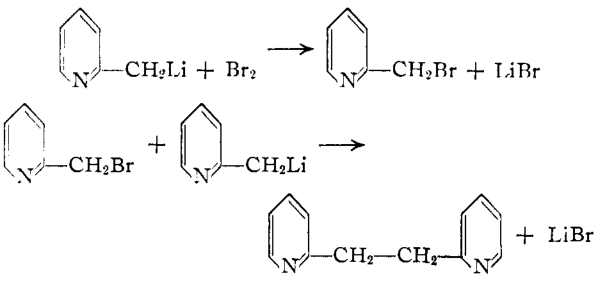
(2) From the M.S. thesis of Paul G. Campbell, University of South Carolina.

(3) W. M. Edwards and P. C. Teague, This Journal, **71**, 3548 (1949).

(4) H. I. Thayer, U. S. Patent 2,496,319, Feb. 7, 1950.

coupling reactions of 2-picolyllithium. Heating this reagent at 110° in toluene or heating with sulfur gave negligible quantities of the coupled product. Addition of iodine gave only black polymeric products. Treatment with cobaltous chloride gave about 17% yield of crude product from which very little pure dipyridylethane could be recovered.

Addition of bromine to a solution of 2-picolyllithium at −40 to −50° resulted in the formation of 1,2-di-(2-pyridyl)-ethane in satisfactory yield. The reaction is believed to take place through the formation of the highly reactive 2-picolyl bromide.



The product was identical with that formed by Thayer's method and with the by-product from the air oxidation of 2-picolyllithium.

Treatment of the dipyridylethane with selenium dioxide and with N-bromosuccinimide gave 1,2-di-(2-pyridyl)-ethene. Oxidation with permanganate gave picolinic acid.

Bergmann[5] found that the 1,2-di-(4-pyridyl)-ethane prepared by Thayer's[6] method using 4-picoline forms solid solutions with the corresponding ethylene compound and the two could not be separated by fractional crystallization. Infrared absorption spectra of the compounds reported here showed that the 1,2-di-(2-pyridyl)-ethane prepared by the action of bromine on 2-picolyllithium was essentially free of the ethylene compound.

Experimental[7]

Coupling with Bromine.—In a typical experiment a solution of 2-picolyllithium prepared from 262 g. (1.67 moles) of bromobenzene, 23.1 g. (3.3 gram atoms) of lithium and 139.5 g. (1.5 moles) of 2-picoline was cooled below −40° in an acetone–Dry Ice-bath. The solution was stirred rapidly and 132 g. (0.825 mole) of bromine was added dropwise over a period of one hour. The temperature was not allowed to rise above −40°. At the end of the addition the color changed sharply from a dark reddish-brown to a light tan. The mixture was stirred an additional hour and then treated with 300 ml. of water followed by 300 ml. of 6 *N* HCl. The ether layer was separated and the aqueous layer was made alkaline with NaOH and extracted with chloroform. The solution was dried and the chloroform and 2-picoline distilled at atmospheric pressure. The fraction boiling at 125–129° at atmospheric pressure was 2-picoline amounting to 29.3 g. Crude dipyridylethane came over at 110 to 130° at 2–5 mm. and a residue of 59.0 g. remained. The crude dipyridylethane was a greenish-yellow solid weighing 54.2 g. Treatment with decolorizing charcoal and recrystallization from petroleum ether gave 38.5 g. of a white product melting at 49.5–50.5°. Mixed melting point with a sample prepared by the method of Thayer (49–50°) gave no depression. The yield of pure product was 27.9% based on the 2-picoline added, or 35.3% based on the 2-picoline consumed. Picrate, m.p. 249.5–250° dec. *Anal.* Calcd. for $C_{12}H_{12}N_2$: N, 15.21; C, 78.22; H, 6.57. Found: N, 15.32; C, 78.01; H, 6.75.

Oxidation with SeO₂.—Selenium dioxide (8.88 g., 0.08 mole) prepared by the wet method of Rabjohn[8] was dissolved in 100 ml. of dioxane and 7.34 g. (0.04 mole) of the dipyridylethane was added. The solution was refluxed for two hours. The product after recrystallization from alcohol melted at 119.5° in agreement with the value reported for 1,2-di-(2-pyridyl)-ethene.[9] *Anal.* Calcd. for $C_{12}H_{10}N_2$: N, 15.38; C, 79.09; H, 5.53. Found: N, 15.46; C, 78.87; H, 5.80.

The same product was obtained by treating the dipyridylethane with N-bromosuccinimide.

Oxidation to Picolinic Acid.—As further proof of the identity of the compound the dipyridylethane was oxidized with permanganate following the procedure in reference 10 for the preparation of picolinic acid from 2-picoline. Picolinic acid hydrochloride, m.p. 210.5–211.5°, was obtained. *Anal.* Calcd. for $C_6H_5O_2N \cdot HCl$: neut. equiv., 79.8; Cl, 22.22. Found: neut. equiv., 80.7; Cl, 22.23.

Infrared Spectra.—The infrared spectra of 1,2-di-(2-pyridyl)-ethane and -ethene in CS_2 solution were obtained. The latter shows a strong absorption peak in 1% solution at 10.27 μ. The absence of any peak at this point for a 5% solution of the ethane indicated that it could not contain more than 0.5% of the unsaturated compound, and probably less.

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[5] E. D. Bergmann, F. E. Crane, Jr., and R. M. Fuoss, This Journal, **74**, 5979 (1952).

[6] H. I. Thayer and B. B. Corson, *ibid.*, **70**, 2331 (1948).

[7] All melting points and boiling points are corrected.

[8] N. Rabjohn, *Org. Reactions*, **5**, 345 (1949).

[9] C. Harries and G. H. Lenart, *Ann.*, **410**, 95 (1915).

[10] *Org. Syntheses*, **20**, 79 (1940).

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Preparations of N,N-Dimethylamides

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RECEIVED NOVEMBER 20, 1953

The customary preparative methods for N,N-dimethylamides involve the reaction of an acid chloride or anhydride and dimethylamine in an inert solvent[1] or in aqueous sodium hydroxide.[2] The use of the somewhat objectionable dimethylamine may be avoided by substituting N,N-dimethylformamide for it. This also permits the elimination of any solvent other than the reactants.

The general procedure consists in heating together the acid chloride or anhydride and N,N-dimethylformamide and separating the mixture by distillation or, in the preparation of amides of high melting point, removal of excess dimethylformamide by distillation followed by recrystallization of the desired product. Whether dimethylformamide or acyl derivative is in excess appears to be of little consequence. Catalytic amounts of sulfuric acid are required when an anhydride is used. Dioxane may be used as solvent, but this does appear to be necessary.

This method was applied to the preparation of a tertiary amine by the reaction of benzyl chloride and dimethylformamide, but the results do not indicate preparative value. Two products were isolated, dimethylbenzylamine and methyldibenzylamine. It is conceived that the latter product was formed from the quaternary salt, dimethyldibenzylammonium chloride, through the loss of the elements of methyl chloride, the quaternary salt

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[1] A. P. N. Franchimont, *Rec. trav. chim.*, **2**, 332 (1883); D. Pressman, J. H. Bryden and L. Pauling, This Journal, **70**, 1354 (1948).

[2] H. Staudinger and N. Kon, *Ann.*, **384**, 114 (1911).