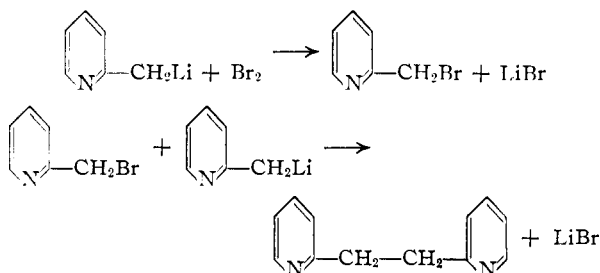


coupling reactions of 2-picolyllithium. Heating this reagent at 110° in toluene or heating with sulfur gave negligible quantities of the coupled product. Addition of iodine gave only black polymeric products. Treatment with cobaltous chloride gave about 17% yield of crude product from which very little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

Bergmann⁵ found that the 1,2-di-(4-pyridyl)-ethane prepared by Thayer's⁶ 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.

Experimental⁷

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%

(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.

based on the 2-picoline consumed. Picrate, m.p. 249.5–250° dec. *Anal.* Calcd. for C₁₂H₁₂N₂: 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 Rabjohn⁸ 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 C₁₂H₁₀N₂: 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 C₆H₅O₂N·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 CS₂ 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.

(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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The customary preparative methods for N,N-dimethylamides involve the reaction of an acid chloride or anhydride and dimethylamine in an inert solvent¹ 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 methyl-dibenzylamine. 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

(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).

arising from the reaction of the dimethylbenzylamine with benzyl chloride. No attempt to isolate the quaternary salt was made.

Experimental

N,N-Dimethylbenzamide.—A mixture of 14.3 g. of benzoyl chloride and 15 g. of N,N-dimethylformamide, b.p. 151–152°, were heated together at 150° for four hours. The product was distilled at reduced pressures and yielded 14.6 g. of N,N-dimethylbenzamide, b.p. 157–158° (35 mm.), m.p. 40–41°, yield 97%.

N,N-Dimethylacetamide.—Acetic anhydride, 20 g., dimethylformamide, 25 g., and one drop of concentrated sulfuric acid were heated under reflux for six hours. The mixture was then distilled. The amount of N,N-dimethylacetamide was 15.7 g. or 92%, b.p. 85–87° (33 mm.), 163–165° (760 mm.).

The yield from a mixture of 10 g. of dimethylformamide and 25 g. of acetic anhydride was 11.2 g. or 94% based upon dimethylformamide.

N,N-Dimethylsuccinamic Acid.—Heating a solution of 10 g. of succinic anhydride in 25 g. of dimethylformamide containing one drop of sulfuric acid permitted the isolation of 13 g. of N,N-dimethylsuccinamic acid following the removal of excess dimethylformamide by distillation and recrystallization from ether; yield 90%, m.p. 79–80°.

Dimethylbenzylamine.—Benzyl chloride, 20 g., and dimethylformamide, 50 g., were heated together for 6 hours at 150°. The mixture was washed with dilute sodium hydroxide solution, extracted with ether and distilled; yield of dimethylbenzylamine 8 g., 36%, b.p. 85–87° (32 mm.); methiodide m.p. 178–179°; yield of methylidibenzylamine 6 g., 34%, b.p. 178–180° (32 mm.); HCl salt m.p. 198–199°.

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Organic Esters of Mannitol Pentanitate¹

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In continuation of the investigation of nitrate esters of polyols,² the acetate, propionate and phenylacetate of *d*-mannitol 1,2,3,5,6-pentanitate have been prepared. A recent publication described the preparation and structural proof of the starting mannitol pentanitate³ and, in addition, gave an excellent bibliography of research on the mannitol system. In the paper by Hayward, *d*-mannitol hexanitate was selectively denitrated by the use of pyridine to *d*-mannitol 1,2,3,5,6-pentanitate in a 73% yield. Previous attempts to prepare this pentanitate by the reaction of mannitol hexanitate and ammonia⁴ and controlled nitration⁵ had given poor yields.

In the present investigation the pyridine method and, in addition, an ammonium carbonate method have been used for selective denitration of mannitol hexanitate. The ammonium carbonate method gave a 70% yield of a mannitol pentanitate that did not depress the melting point of the pentanitate prepared by the pyridine method. It was found that the acetate, propionate and phenylacetate of mannitol pentanitate readily could be prepared from the corresponding acid chloride and mannitol pentanitate.

(1) This work was performed at Allegany Ballistics Laboratory, an establishment owned by the U. S. Navy and operated by Hercules Powder Company under Contract NOrd 10431.

(2) N. S. Marans, D. E. Elrick and R. F. Preckel, *THIS JOURNAL*, **76**, 1304 (1954).

(3) L. D. Hayward, *ibid.*, **73**, 1974 (1951).

(4) Tichanowitsch, *Z. chem. Pharm.*, 482 (1864).

Determination of the neutral equivalent for mannitol acetate pentanitate, mannitol propionate pentanitate and mannitol hexanitate indicated rapid quantitative hydrolysis. For both mannitol phenylacetate pentanitate and mannitol pentanitate the saponification was slower, but no effort was made to isolate the products of these saponifications.

Experimental

Mannitol Pentanitate.—Mannitol was nitrated to mannitol hexanitate by the use of 100% nitric acid or mixed nitric and sulfuric acids by essentially the method of Patterson and Todd.⁵ Mannitol hexanitate, m.p. 111–112°, was converted to mannitol pentanitate by the use of pyridine.³ This synthesis was also accomplished in the following manner. A mixture of 0.0166 mole of mannitol hexanitate, 0.019 mole of ammonium carbonate, 40 ml. of acetone and 5 ml. of water was allowed to stand for 16 hours at 25°. Most of the acetone was removed by evacuation and then ethanol-water added to precipitate the crude pentanitate. The crude product was recrystallized from ethanol-water to give 0.0115 mole (70%) of mannitol pentanitate, m.p. 80–81° (lit. m.p. 81–82°).³ This material did not depress the melting point of the pentanitate obtained from the pyridine reaction.

Mannitol Acetate Pentanitate.—A mixture of 0.0065 mole of mannitol pentanitate and 0.1 mole of acetyl chloride was heated in a flask for two hours at 65° with progress of the reaction evidenced by evolution of hydrogen chloride. The mixture was neutralized with aqueous sodium bicarbonate and the organic layer recrystallized from ether-carbon tetrachloride to give 0.0055 mole (85%) of mannitol acetate pentanitate, m.p. 77–78°. This material depressed the m.p. of mannitol pentanitate. No proof of the final configuration was made.

Anal. Calcd. for C₈H₁₁O₁₇N₅: C, 21.38; H, 2.45; N, 15.59; mol. wt., 449. Found: C, 22.00; H, 2.50; N, 15.35; mol. wt. by cryoscopic method (benzene), 425.

Mannitol Propionate Pentanitate.—A mixture of 0.0027 mole of mannitol pentanitate and 0.1 mole of propionyl chloride was heated in a flask at 80° for one hour. The mixture was neutralized with aqueous sodium bicarbonate and extracted with ether. Isolation of the product from the ether was accomplished by concentration of the ethereal layer and the addition of carbon tetrachloride. By this method there was obtained 0.0019 mole (70%) of mannitol propionate pentanitate, m.p. 65–68°.

Anal. Calcd. for C₉H₁₃O₁₇N₅: C, 23.33; H, 2.81; N, 15.12; mol. wt., 463. Found: C, 23.98; H, 2.74; N, 14.97; mol. wt. by cryoscopic method (benzene), 463.

Mannitol Phenylacetate Pentanitate.—A solution of 0.0078 mole of mannitol pentanitate and 0.058 mole of phenylacetyl chloride was stirred for 18 hours at 25°. The final solution was washed with aqueous sodium bicarbonate and then recrystallized from acetone-ethanol-water to give 0.0053 mole (68%) of mannitol phenylacetate pentanitate, m.p. 61–62°.

Anal. Calcd. for C₁₄H₁₈O₁₇N₅: C, 32.00; H, 2.86; N, 13.33; mol. wt., 525. Found: C, 32.04; H, 2.88; N, 13.16; mol. wt. by cryoscopic method (benzene), 500.

Saponification of this ester with dilute sodium hydroxide gave, after acidification of the reaction mixture, 60% of the theoretical phenylacetic acid, identified by melting point and mixed melting point.

Neutral Equivalents of Mannitol Derivatives.—Neutral equivalents were determined for the acetate, propionate and phenylacetate of mannitol pentanitate and for mannitol pentanitate and hexanitate. The method used was solution of the nitrate in acetone, addition of excess standard sodium hydroxide (more than required for saponification of all ester groupings in the molecule) and back titration after varying periods of time with standard hydrochloric acid to a neutral solution, using brom thymol blue as an indicator. For the mannitol acetate pentanitate a neutral equivalent of 78.6 (five minutes) and 77.0 (ten minutes)

(5) T. S. Patterson and A. R. Todd, *J. Chem. Soc.*, 2876 (1929).

(6) All melting points were determined on a Fisher-Johns melting point block and were uncorrected.