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 methyldibenzylamine 6 g., 34%, b.p. 178-180° (32 mm.); HCl salt m.p. 198-199°.

THE RICE INSTITUTE
HOUSTON 1, TEXAS

---

## Organic Esters of Mannitol Pentanitrate[1]

BY D. E. ELRICK, N. S. MARANS AND R. F. PRECKEL

RECEIVED SEPTEMBER 17, 1953

In continuation of the investigation of nitrate esters of polyols,[2] the acetate, propionate and phenylacetate of *d*-mannitol 1,2,3,5,6-pentanitrate have been prepared. A recent publication described the preparation and structural proof of the starting mannitol pentanitrate[3] and, in addition, gave an excellent bibliography of research on the mannitol system. In the paper by Hayward, *d*-mannitol hexanitrate was selectively denitrated by the use of pyridine to *d*-mannitol 1,2,3,5,6-pentanitrate in a 73% yield. Previous attempts to prepare this pentanitrate by the reaction of mannitol hexanitrate and ammonia[4] and controlled nitration[3] 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 hexanitrate. The ammonium carbonate method gave a 70% yield of a mannitol pentanitrate that did not depress the melting point of the pentanitrate prepared by the pyridine method. It was found that the acetate, propionate and phenylacetate of mannitol pentanitrate readily could be prepared from the corresponding acid chloride and mannitol pentanitrate.

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

### Experimental

**Mannitol Pentanitrate.**—Mannitol was nitrated to mannitol hexanitrate by the use of 100% nitric acid or mixed nitric and sulfuric acids by essentially the method of Patterson and Todd.[5] Mannitol hexanitrate, m.p. 111-112°, was converted to mannitol pentanitrate by the use of pyridine.[3] This synthesis was also accomplished in the following manner. A mixture of 0.0166 mole of mannitol hexanitrate, 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 pentanitrate. The crude product was recrystallized from ethanol-water to give 0.0115 mole (70%) of mannitol pentanitrate, m.p. 80-81°[6] (lit. m.p. 81-82°).[3] This material did not depress the melting point of the pentanitrate obtained from the pyridine reaction.

**Mannitol Acetate Pentanitrate.**—A mixture of 0.0065 mole of mannitol pentanitrate 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 pentanitrate, m.p. 77-78°. This material depressed the m.p. of mannitol pentanitrate. No proof of the final configuration was made.

*Anal.* Calcd. for $C_8H_{11}O_{17}N_5$: 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 Pentanitrate.**—A mixture of 0.0027 mole of mannitol pentanitrate 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 pentanitrate, m.p. 65-68°.

*Anal.* Calcd. for $C_9H_{13}O_{17}N_5$: 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 Pentanitrate.**—A solution of 0.0078 mole of mannitol pentanitrate 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 pentanitrate, m.p. 61-62°.

*Anal.* Calcd. for $C_{14}H_{15}O_{17}N_5$: 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 pentanitrate and for mannitol pentanitrate and hexanitrate. 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 pentanitrate a neutral equivalent of 78.6 (five minutes) and 77.0 (ten minutes)

---

[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).

[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.

was obtained, compared to 74.8 for complete hydrolysis of all ester groups. For mannitol propionate pentanitrate after two hours a neutral equivalent of 75.0 was obtained, compared to 77.2 for complete hydrolysis. For mannitol hexanitrate the neutral equivalent after five minutes was 74.4, compared to 75.4 for complete hydrolysis. In the case of mannitol pentanitrate, however, a five-minute period gave 129 for a neutral equivalent and a 30-minute period 126, compared to a value of 81.6 for all five ester groups hydrolyzed, 102 for four and 136 for three. For mannitol phenylacetate pentanitrate an average value of 168 was obtained after five minutes and 113 after 15 minutes, compared to 178.3 for three groups hydrolyzed, 131.2 for four, 105 for five and 87.5 for six.

**Acknowledgment.**—The authors wish to express their thanks to Dr. L. G. Bonner for his advice during the course of these investigations. The analyses reported were done by Micro-Tech Laboratories, Skokie, Illinois.

ALLEGANY BALLISTICS LABORATORY
HERCULES POWDER COMPANY
CUMBERLAND, MARYLAND

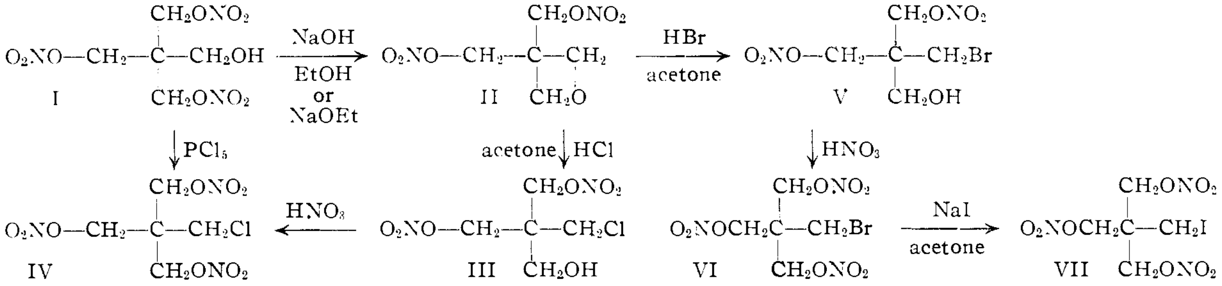
## Preparation of Halides of Pentaerythritol Trinitrate[1]

BY D. E. ELRICK, W. H. GARDNER, N. S. MARANS AND R. F. PRECKEL

RECEIVED SEPTEMBER 17, 1953

In a preceding paper the preparation of pentaerythritol trinitrate (I) and related organic esters was described.[2] In the present investigation, the chloride, bromide and iodide of pentaerythritol trinitrate have been synthesized and their chemical reactivities investigated.

The synthesis of the chloride IV was accomplished by two different methods: (1) the reaction of phosphorus pentachloride and pentaerythritol trinitrate (I) to give the desired chloride and (2) the reaction of pentaerythritol trinitrate and sodium ethylate or alcoholic sodium hydroxide to give 3,3-bis-(nitratomethyl)-oxetane[3] (II), the cleavage of the oxetane with hydrochloric acid to give pentaerythritol chloride dinitrate (III), and the subsequent nitration of the dinitrate to give the desired product IV. The bromide VI was synthesized by the cleavage of the cyclic ether II with hydrobromic acid to give pentaerythritol bromide dinitrate V and subsequent nitration to the trinitrate; the iodide VII was prepared by the reaction of pentaerythritol bromide trinitrate and sodium iodide in acetone.



The halides of pentaerythritol trinitrate were not attacked readily by nucleophilic or electrophilic reagents as shown by their lack of reactivity with such reagents as silver nitrate, lead nitrate, silver cyanide, sodium cyanide and sodium hydroxide. The alkaline hydrolysis of these halides did not give specific cleavage of the non-nitrate substituent as in the case of the organic esters of pentaerythritol trinitrate.[2]

### Experimental

**3,3-Bis-(nitratomethyl)-oxetane.**—Pentaerythritol trinitrate,[2] 0.1 mole, and freshly prepared sodium ethylate, 0.1 mole, in 100 ml. of absolute ethanol were heated at 70° for eight hours to give a neutral mixture. On filtration of the mixture, a solid precipitate was obtained and the water-soluble portion discarded. The filtrate was concentrated to 20 ml. by evacuation and the solid that crystallized was filtered and added to the previously obtained water-insoluble solid. On recrystallization from carbon tetrachloride by successive evaporations of the solvent, there was obtained 0.0155 mole (15.5%) of 3,3-bis-(nitratomethyl)-oxetane, m.p. 89–91°.[4] Other isolated products of the reaction included pentaerythritol trinitrate and lower nitrates. Similar yields of the oxetane were obtained when alcoholic sodium hydroxide replaced sodium ethylate.

*Anal.* Calcd. for $C_5H_8O_7N_2$: C, 28.84; H, 3.85; N, 13.46. Found: C, 28.80; H, 3.91; N, 13.26.

Treatment of the cyclic ether with additional sodium ethylate gave complete denitration.

**Pentaerythritol Chloride Dinitrate.**—To 0.024 mole of 3,3-bis-(nitratomethyl)-oxetane dissolved in 50 g. of acetone there was added with stirring 37.5 g. of concentrated hydrochloric acid. After being stirred at 25° for one hour, the reaction mixture was added to water and the organic layer separated, washed with water, with aqueous sodium bicarbonate and again with water. The organic layer was dried by evacuation to give a 38% yield of pentaerythritol monochloride dinitrate.

*Anal.* Calcd. for $C_5H_9O_7N_2Cl$: C, 24.54; H, 3.68; N, 11.45; Cl, 14.52. Found: C, 24.83; H, 3.87; N, 10.92; Cl, 14.35.

**Pentaerythritol Chloride Trinitrate. A. From Pentaerythritol Chloride Dinitrate.**—To 0.80 mole of anhydrous nitric acid cooled to −10° and air agitated in a test-tube there was added 0.0058 mole of pentaerythritol chloride dinitrate. Air agitation was continued for one hour after the addition and the nitric acid solution was then added to ice and filtered to give 0.0053 mole (91%) of pentaerythritol chloride trinitrate. Recrystallization from an ethanol-water solution gave a white crystalline solid, m.p. 65–66°.

*Anal.* Calcd. for $C_5H_8O_9N_3Cl$: C, 20.73; H, 2.76; N, 14.51. Found: C, 20.85; H, 2.89; N, 14.52.

B. **From Pentaerythritol Trinitrate.**—A mixture of 0.022 mole of pentaerythritol trinitrate and 0.023 mole of phos-

---

[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 E. F. Preckel, THIS JOURNAL, **76**, 1304 (1954).

[3] A similar type of cyclization has been reported for the reaction of monobromopentaerythritol and potassiun hydroxide to give 3,3-bis-(hydroxymethyl)-oxetane, by Beyaert and Govaert, *Proc. Acad. Sci. Amsterdam*, **42**, 790 (1939). In addition, glycerol dinitrate and sodium hydroxide give 3-nitratoglycide; P. Naoum translated by E. M. Symmes, "Nitroglycerin and Nitroglycerin Explosives," The Williams and Wilkins Co., Baltimore, Md., 1928, p. 168.

[4] All melting points were determined on a Fisher-Johns melting point block and were uncorrected.