

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.

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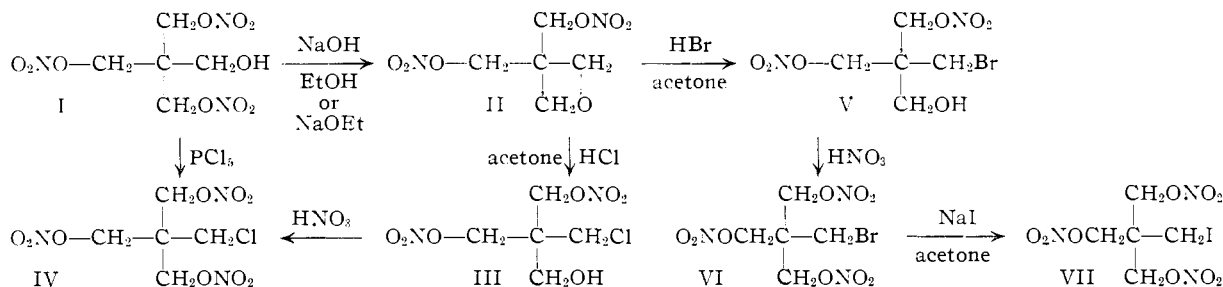
Preparation of Halides of Pentaerythritol Trinitrate¹

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

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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)-oxetane³ (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 syn-

(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 potassium 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.

thesized 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 C₅H₈O₇N₂: 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 C₅H₈O₇N₂Cl: 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 C₅H₈O₉N₃Cl: 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-

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

phorus pentachloride gave an exothermic reaction five minutes after mixing. Alternate cooling and shaking permitted control of the reaction, and the mixture was heated to 80° for ten minutes to complete the reaction. After an additional three hours at 25° (longer periods of time gave extensive carbonization), the mixture was washed with aqueous sodium bicarbonate and extracted with ether. Removal of the ether by evacuation and recrystallization of the crude product from cold ethanol-water gave 0.0049 mole (22.3%) of pentaerythritol chloride trinitrate, m.p. 60–62°. A further recrystallization from the same solvent gave m.p. 61–62°, mixed m.p. 63–64°.

Pentaerythritol Bromide Dinitrate.—3,3-Bis-(nitratomethyl)-oxetane, 8 g., was dissolved in acetone, 80 ml., and 48% hydrobromic acid, 48 g., was added slowly with stirring in ten minutes. The solution after standing for an additional ten minutes was added to 300 ml. of water and the organic layer separated and evacuated to give 8.15 g. (81.5%) of pentaerythritol bromide dinitrate, a liquid, n_D^{20} 1.5095.

Anal. Calcd. for $C_5H_8O_7N_2Br$: C, 20.77; H, 3.12; N, 9.69. Found: C, 21.17; H, 3.30; N, 9.36.

Pentaerythritol Bromide Trinitrate.—Pentaerythritol bromide dinitrate, 7.7 g., was added slowly with air agitation in 20 minutes to 30 g. of almost water-white 100% nitric acid at –5°. The air agitation was continued for 90 minutes at –5° and the reaction mixture then poured into ice and water. The precipitate was filtered and washed with water, 5% aqueous sodium bicarbonate and then water to give 8.2 g. (91%) of crude material. Recrystallization from hot ethanol gave white crystals, m.p. 89–90°.

Anal. Calcd. for $C_5H_8O_9N_3Br$: C, 17.97; H, 2.40; N, 12.58. Found: C, 18.30; H, 2.36; N, 12.58.

Pentaerythritol Iodide Trinitrate.—A solution of 2.00 g. of pentaerythritol bromide trinitrate, 1.00 g. of potassium iodide and 50 g. of anhydrous acetone was refluxed for two hundred hours. The potassium bromide was removed by filtration and the filtrate evaporated to give 0.92 g. (41%) of pentaerythritol iodide trinitrate, m.p. 108.5–110.5°. Shorter reaction times gave mixtures of the iodide and bromide.

Anal. Calcd. for $C_5H_8O_9N_3I$: C, 15.75; H, 2.10; N, 11.02. Found: C, 15.97; H, 2.19; N, 10.84.

Reactions of Halides of Pentaerythritol Trinitrate.—The following attempted reactions gave 70–100% recovery of the unreacted pentaerythritol halide trinitrate. In all cases the reaction mixture was refluxed for 40–120 hours: (1) pentaerythritol bromide trinitrate and silver nitrate in ethanol or acetonitrile, (2) pentaerythritol chloride trinitrate and silver nitrate in ethanol, (3) pentaerythritol bromide trinitrate and lead nitrate in ethanol, (4) pentaerythritol chloride trinitrate and potassium iodide in acetone and (5) pentaerythritol bromide trinitrate and silver cyanide in absolute ethanol.

The refluxing of a solution of pentaerythritol bromide trinitrate and sodium cyanide in 95% ethanol for five hours gave a 50% recovery of the halide and no other water-insoluble products. A similar reaction was obtained with sodium ethylate. With these reagents the pentaerythritol bromide trinitrate appeared to undergo alkaline hydrolytic reactions.

Hydrolysis of Pentaerythritol Trinitrate Halides.—To a solution of 0.8×10^{-3} mole of pentaerythritol chloride trinitrate in 40 ml. of acetone there was added a measured excess of standard sodium hydroxide. After one hour the solution was back-titrated with nitric acid, and it was found that 1.96×10^{-4} mole of sodium hydroxide had been consumed. The solution was ether extracted, and the aqueous layer on analysis for chloride ion by the silver chloride method gave a value of 4.1×10^{-5} mole. This indicated that equivalent quantities of nitrate and chloride groups had been hydrolyzed. The same procedure for pentaerythritol bromide trinitrate, 2.9×10^{-3} mole, gave 4.5×10^{-4} mole of sodium hydroxide required and 1.17×10^{-4} mole of silver bromide formed. This was similar to the chloride.

Acknowledgment.—The authors wish to acknowledge the advice of Dr. L. G. Bonner during this problem. All analyses were done by Micro-Tech Laboratories, Skokie, Illinois.

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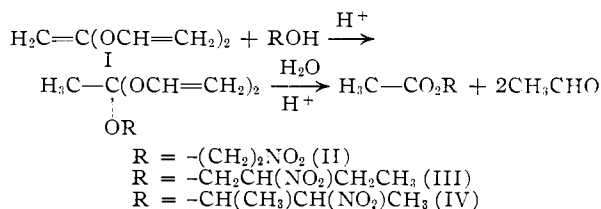
The Reaction of Ketene Divinylacetal with Various Nitro Compounds^{1,2}

BY HENRY FEUER AND WILLIAM H. GARDNER

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The preparation and reactions of ketene divinylacetal (I) have recently been reported by McElvain.³ Compound I reacted with ethanol and 2-chloroethanol in the presence of catalytic amounts of acid to give the corresponding divinyl orthoacetates and with hydrogen chloride to form 1,1-divinyloxy-1-chloroethane.

This investigation consists of a study of addition reactions of nitro alcohols and nitro paraffins with ketene divinylacetal. 2-Nitroethanol, 2-nitro-1-butanol and 3-nitro-2-butanol reacted readily with I to form the corresponding divinyl nitroalkyl-orthoacetates (II, III and IV). These orthoac-



tates were high boiling liquids whose structures were established by elementary analysis and by hydrolysis to the corresponding nitroalkyl acetates.

The orthoacetates (II and III) were readily polymerized, by heating alone or in the presence of benzoyl peroxide, to dark viscous liquids from which solid polymers were obtained by dissolution in acetone and precipitation into cold water. The elemental analyses of these polymers did not agree with any simple structure.

In contrast to compounds II and III, divinyl 3-nitro-2-butyl orthoacetate (IV) did not polymerize.

It was anticipated that nitro paraffins would be acidic enough to add to ketene divinylacetal in a manner similar to hydrogen chloride.³ Nitromethane and 1,1-dinitroethane failed to react under acidic or basic conditions even though reflux temperatures were used. Only starting materials were recovered.

Experimental

Divinyl β -Nitroethyl Orthoacetate (II).—Six grams (0.053 mole) of ketene divinylacetal was placed in a 50-ml. distilling flask, immersed in an ice-bath and acidified with 2 drops of a solution of hydrochloric acid in nitroethanol (0.1 g. of concd. hydrochloric acid per ml. of nitroethanol). Then 4.8 g. (0.053 mole) of nitroethanol was added dropwise with stirring. The reaction was continued for 30 minutes and then the mixture was distilled under reduced pressure. A fraction of divinyl nitroethyl orthoacetate amounting to 5.6 g. (52%) was collected, b.p. 80–85° at 2 mm., n_D^{25} 1.4492.

Anal. Calcd. for $C_5H_{13}NO_5$: C, 47.29; H, 6.40; N, 6.89. Found: C, 47.31; H, 6.40; N, 7.10.

Divinyl 2-Nitro-1-butyl Orthoacetate (III).—The same procedure was used for the preparation of this compound as

(1) Taken in part from the M.S. thesis of William H. Gardner, Purdue University, June, 1952.

(2) Financial support of this research was in part supplied by the United States Office of Naval Research.

(3) S. M. McElvain and A. N. Bolstad, *THIS JOURNAL*, **73**, 1988 (1951).