

dibromide of m.p. 73.7–75.7° (lit.¹⁵ m.p. 73°). In addition, there remained in the distillation flask 5.62 g. of polymeric material which if assumed to be polystyrene brings the total yield of styrene to 58%. Fraction 2 was unchanged XVII (39%). The original amine had a boiling point of 86–87° (9 mm.) and n_D^{20} 1.5032. The methiodide melted at 230–232° (lit.¹⁶ m.p. 227°).

A smaller high-boiling fraction was obtained when the bath was heated to 205° (1.9 mm.). It had n_D^{20} 1.5118 and weighed 0.23 g. (2.0%). This material was identified as N-methyl-bis- β -phenethylamine as the hydrochloride which melted at 162–164° (lit.¹⁷ m.p. 160°).

Mixed Disproportionation of N,N-Dimethylbenzylamine (II) and N,N-Dimethyl-2-thenylamine (VII).—In the apparatus used for the disproportionation of VII as described above were mixed II (6.76 g., 0.05 mole), benzyltrimethylammonium iodide (1.39 g., 0.005 mole), VII (7.06 g., 0.05 mole) and 2-thenyltrimethylammonium iodide (1.42 g., 0.005 mole), and the mixture was heated 18 hours at an oil-bath temperature of 195–198°. The liquid which collected in the trap was shown to be trimethylamine by its conversion to a picrate which showed no depression in its melting point when mixed with authentic trimethylamine picrate.

The reaction mixture was extracted with dry ether leaving 1.9 g. of a pale yellow solid which was apparently a mixture of tetramethylammonium iodide and those methiodides initially present. After removal of the solvent, the residual liquid was distilled into several fractions. Those which contained mixtures of I, VIII and XXIII were combined and redistilled. The middle fraction was used to prepare an analytical sample of boiling point 180° (18 mm.) and n_D^{20} 1.5716 (lit.¹⁸ 148–152° (12 mm.)).

(15) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 261.

(16) T. B. Johnson and H. H. Guest, *Am. Chem. J.*, **42**, 348 (1909).

(17) F. Kulz, K. W. Rosenmund, *et al.*, *Ber.*, **72**, 2161 (1939).

(18) J. V. Braun, R. Fussganger and M. Kuhn, *Ann.*, **445**, 201 (1925).

Anal. Calcd. for $C_{13}H_{16}NS$: C, 71.84; H, 6.96; N, 6.45. Found: C, 72.05; H, 6.74; N, 6.26.

The result of the analysis indicates that some N-methyl-N-benzyl-2-thenylamine was formed during the reaction. However, the boiling points of I, VIII and XXIII are too close together for easy separation of the compounds and consequently no per cent. yield was determined.

Mixed Disproportionation of N,N-Dimethylbenzylamine (II) and N,N-Dimethylfurfurylamine (V).—A mixture of II (10.29 g., 0.076 mole), V (9.5 g., 0.076 mole) and methyl iodide (1.96 g., 0.014 mole) were mixed and heated at an oil-bath temperature of 170–190° for twenty and one-third hours. The reaction mixture was distilled *in vacuo* and separated into the following fractions.

Fraction	°C.	B.p. Mm.	n_D^{20}	Wt., g.
1	52.5–64	15	1.4687	1.03
2	66–71	15	1.4994	1.57
3	66–71	0.3	1.5143	1.72
4	73–78	0.3	1.5274	1.27
5	79–82	0.3	1.5382	3.35
6	97–108	0.75	1.5516	2.22

Fraction 1 was somewhat impure V, fraction 2 impure II, fraction 3 impure VI and fraction 6 impure I.

Fraction 5 was N-methyl-N-benzylfurfurylamine (22%). It was redistilled for analysis and had a boiling point of 82° (0.4 mm.) and a n_D^{20} 1.5367.

Anal. Calcd. for $C_{13}H_{15}ON$: C, 77.58; H, 7.51; N, 6.96. Found: C, 78.12; H, 7.92; N, 7.18.

A methiodide was prepared which melted at 135–135.4° (lit.¹⁸ 135°).

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[CONTRIBUTION FROM THE HERCULES POWDER CO., ALLEGANY BALLISTICS LABORATORY]

Organic Acid Esters of Pentaerythritol Trinitrate¹

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A series of organic acid esters of pentaerythritol trinitrate have been prepared by various esterification techniques. These esters are similar to the 2-nitratoethyl esters in their reactivity with dilute base.

Compounds containing the pentaerythritol trinitrate grouping have been mentioned only briefly in the literature. The preparation of several organic acid esters and ethers of pentaerythritol trinitrate was claimed in a patent,² but no description of the synthetic methods used or of the physical properties of the compounds obtained were given. A recent paper³ described the preparation of a number of ethers of pentaerythritol and their nitration products.

Organic acid esters of pentaerythritol trinitrate were desired for comparison of their chemical reactivity with previously synthesized 2-nitratoethyl esters.⁴ In both cases, only primary nitrate groups are present. The synthesis of the pentaerythritol trinitrate esters was accomplished by esterification of pentaerythritol trinitrate with acids, acid chlorides or acid anhydrides. Pentaerythritol trini-

trate was prepared by nitration of pentaerythritol monoacetate⁵ to give the corresponding trinitrate which in turn was subjected to controlled saponification to give the desired trinitratoalcohol.

Controlled saponification of the pentaerythritol acetate trinitrate showed the typical preferential cleavage of the organic ester linkage rather than that of the nitrate ester linkage under alkaline conditions. This was in accordance with previous work on the controlled saponification of 2-nitratoethyl crotonate.⁴ In general the prepared series of esters of pentaerythritol trinitrate gave this same cleavage as shown by their neutral equivalents. A few exceptions to this rapid and quantitative hydrolysis of the organic ester linkage were noted, however. The phthalate ester hydrolyzed more slowly than other organic esters and the benzene-sulfonate and *p*-toluenesulfonate esters were saponified at a rate equivalent to that of pentaerythritol trinitrate. The esterification of pentaerythritol

(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) German Patents 638,432 and 638,433 (1936).

(3) R. Evans and J. A. Gallagher, *THIS JOURNAL*, **75**, 1248 (1953).

(4) N. S. Marans and R. P. Zelinski, *ibid.*, **72**, 5330 (1950).

(5) R. H. Barth and H. Burrell, U. S. Patent 2,356,745 (Aug. 29, 1944). This patent described the preparation of pentaerythritol diacetate and triacetate only.

trinitrate was accomplished with varying ease. It was found that esterification of pentaerythritol trinitrate with formic or acetic acid in the presence of an acid catalyst proceeded readily at 25°. Attempted duplication of this reaction for propionic, chloroacetic and benzoic acids was unsuccessful. The other two methods of esterification of this alcohol were the use of acid chlorides and pentaerythritol trinitrate with or without an acid acceptor and the use of an acid anhydride and the trinitratoalcohol with either an acid catalyst or an acid acceptor. By the first of these latter two methods most of the desired esters were prepared. Usually the reaction of the acid chloride and pentaerythritol trinitrate alone was sufficient to give the desired ester, but for the preparation of diesters of dibasic acids, it proved desirable to use the acid chloride in the presence of pyridine to ensure more rapid and complete reaction. The use of the acid anhydride in the presence of sulfuric acid or pyridine to esterify pentaerythritol trinitrate proved successful in the few cases in which this method was attempted, but work was limited because these anhydrides were not readily available.

For the preparation of chloroacetates of pentaerythritol trinitrate, esterification of pentaerythritol trinitrate with chloroacid chlorides appeared to become more difficult with increasing substitution of chlorine atoms on the alpha carbon. For example, pentaerythritol acetate trinitrate was readily prepared from the acid chloride and pentaerythritol trinitrate with or without pyridine, while pentaerythritol chloroacetate trinitrate was prepared only with difficulty under similar conditions. The dichloroacetate and trichloroacetate could not be isolated at all in this manner. In cases where the esterification occurred only with difficulty or not at all in the presence of an acid catalyst, pentaerythritol tetranitrate was formed in small quantities, evidently as a product of a redistribution reaction. This was illustrated by the reaction of trichloroacetyl chloride and pentaerythritol trinitrate and the role of acid in this type of reaction is illustrated by the considerable quantity of pentaerythritol tetranitrate formed during the reaction of pentaerythritol trinitrate and sulfuric acid.

Experimental

Materials.—Succinyl,⁶ oxalyl,⁷ *o*-nitrobenzoyl⁸ and 4-chloro-3-nitrobenzoyl chlorides⁸ were prepared from the acids. All other reagents were the best grades available from Eimer and Amend, Fisher Scientific Company or Eastman Kodak Company.

Preparation of Pentaerythritol Trinitrate. A. Pentaerythritol Monoacetate.—Pentaerythritol (80 g.) and pentaerythritol tetraacetate (59 g.) were heated in the presence of 1 g. of potassium carbonate for 16 hours at 180–185°. The reaction mixture was distilled, b.p. 160–205° (2–4 mm.), to give a mixture of products. Separation of the mixed pentaerythritol esters was accomplished in the following manner. Treatment of the distillate with 500 ml. of hot acetone and filtration of the mixture gave 48.3 g. of pentaerythritol, m.p. 258–260°,⁹ mixed m.p. 258–260°. The fil-

trate was distilled under reduced pressure to a volume of 200 ml. and then 100 ml. of ether added. After standing for 20 hours an additional 1 g. of pentaerythritol was removed by filtration. The filtrate was then evacuated to remove the volatile solvent and the crude product treated with 300 ml. of ether to give 34.5 g. of pentaerythritol monoacetate, m.p. 65–66°. Two recrystallizations of this product from ethylene chloride gave a m.p. 69.5–70.0°. Evaporation of the ethereal filtrate gave a liquid which was shown by nitration to contain 20 g. of pentaerythritol monoacetate and 30 g. of higher acetates of pentaerythritol. The total yield of pentaerythritol monoacetate based on reacted pentaerythritol was 71.7% (54.5 g.). For intermediate isolation of the monoacetate, it was found necessary to distill the reaction mixture because pentaerythritol monoacetate could not be readily crystallized from an undistilled mixture.

Anal. Calcd. for C₇H₁₄O₅: C, 47.19; H, 7.87. Found: C, 47.02; H, 7.99.

B. Pentaerythritol Acetate Trinitrate.—Pentaerythritol monoacetate (5.0 g.) was added with air-sparging over a period of five minutes to 60 g. of 100% nitric acid (90% nitric acid could also be used) cooled to 0°. After two hours of agitation at 0°, the nitric acid solution was added to ice and water and the white solid that formed was filtered and washed with copious quantities of water. This solid on recrystallization from hot ethanol gave 8.8 g. (99%) of pentaerythritol acetate trinitrate. Successive recrystallizations from ethanol gave a m.p. 87–88°.

Anal. Calcd. for C₇H₁₁O₁₁N₃: C, 26.83; H, 3.52; N, 13.42. Found: C, 27.07; H, 3.65; N, 13.32.

C. Pentaerythritol Trinitrate.—A solution of pentaerythritol monoacetate trinitrate (30.0 g.) in 100 g. of acetone was added to a solution of 5.0 g. of sodium hydroxide in 50 g. of water, and then 50 g. of ethanol was added to give solution. After 30 minutes the reaction mixture was neutralized with 1 *N* hydrochloric acid and most of the solvent removed by evaporation. The separated organic layer was washed twice with water and evacuated at 10 mm. for six hours to give 21.5 g. (93.6%) of a very viscous oil which could be crystallized from water at 0° to give a solid, m.p. 26–28°. The over-all yield based on reacted pentaerythritol was 65%.

Anal. Calcd. for C₈H₈O₁₀N₃: C, 22.14; H, 3.32; N, 15.48. Found: C, 22.66; H, 3.61; N, 15.62.

The preparation of pentaerythritol trinitrate was accomplished in most cases without isolation of intermediate products. The mixture of crude products from the equilibration of pentaerythritol and pentaerythritol tetraacetate was nitrated with either 90 or 100% nitric acid, and the resultant mixture of pentaerythritol tetranitrate and pentaerythritol acetate trinitrate was separated by the insolubility of the tetranitrate in warm ethanol. The pentaerythritol acetate trinitrate was carefully saponified as in the above synthesis to give pentaerythritol trinitrate. In some instances the crude nitration product was saponified and the pentaerythritol tetranitrate removed by its insolubility in ethanol. Removal of the ethanol by evacuation from the filtrate and washing with water of the resultant organic layer gave pentaerythritol trinitrate. These methods gave yields comparable to those obtained when the intermediate products were isolated.

Preparation of Esters of Pentaerythritol Trinitrate.—Seven general methods were employed for esterification of pentaerythritol trinitrate. Methods A and B utilized the organic acid, C, D and E the acid chloride, and F and G the acid anhydride. A specific illustration is given for each of the general methods. Preparations are summarized in Table I.

Method A.—A mixture of 100 g. of pentaerythritol trinitrate, 100 g. of 90% formic acid, 100 g. of benzene and 3 g. of concd. sulfuric acid was allowed to stand at 25° for three hours. Evaporation of the benzene yielded a white solid which, on recrystallization from hot ethanol, gave 92.7 g. (84.1%) of pentaerythritol formate trinitrate, m.p. 62–63°.

Method B.—Concentrated sulfuric acid (2 g.) was added carefully to a solution of 20 g. of pentaerythritol trinitrate and 20 g. of acetic acid. After standing for two hours at 25°, the white solid was washed with water and recrystallized from hot ethanol to give 13.8 g. (60%) of pentaerythritol acetate trinitrate, m.p. 87–88°.

Method C.—To a solution of 110 g. of pentaerythritol trinitrate in 50 g. of ether in a three-necked flask in a water-

(6) T. Curtius and W. Hechtenberg, *J. prakt. Chem.*, **105**, 302 (1922).

(7) H. Staudinger, *Ber.*, **41**, 3563 (1908).

(8) H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 147.

(9) All melting points were taken on a Fisher-Johns apparatus and were uncorrected.

TABLE I
 ESTERS OF PENTAERYTHRITOL TRINITRATE

	Ester prepared	Method ^a	Yield, %	M.p., °C.	Carbon		Hydrogen		Analyses, %		Neut. equiv.	
					Calcd.	Found	Calcd.	Found	Calcd.	Nitrogen Found	Calcd.	Found
I	Formate	A	84	60-61	24.08	24.20	3.01	3.28	14.05	13.77	299	300
II	Acetate	B, C, F, G	60, 70, 78, 94	87-88	26.83	27.07	3.51	3.65	13.42	13.32	313	310
III	Propionate	C	83	39-40	29.36	29.51	3.98	4.15	12.84	12.54	327	328
IV	Valerate	D	65	Liquid	33.80	34.50	4.80	4.92	11.84	11.95		
V	Caproate	C, D	50, 50	Liquid	35.77	35.82	5.15	5.30	11.38	11.48		
VI	Chloroacetate	C, D	10, 15	52-53	24.17	24.00	2.88	3.16	12.09	12.03	347.5	354
VII	Oxalate	D	22	97-100	24.16	24.88	2.68	3.00	14.09	13.67		
VIII	Succinate	C, D	41, 52	88-90	26.92	27.17	3.21	3.29	13.46	13.20	312	302
IX	Adipate	D	45	82-83	29.45	30.03	3.68	3.92	12.88	12.22	326	327
X	Benzoate	E	61	89-90	38.40	38.91	3.47	3.61	11.20	11.42	375	376
XI	Phthalate	D	68	115-117	32.14	32.40	2.98	3.02	12.50	11.90	336	501
XII	<i>o</i> -Nitrobenzoate	D	64	94-95	34.29	34.42	2.86	2.80	13.33	13.32	420	426
XIII	<i>m</i> -Nitrobenzoate	D	71	102-103	34.29	34.54	2.86	3.12	13.33	13.36	420	419
XIV	<i>p</i> -Nitrobenzoate	D	60	106-108	34.29	34.43	2.86	2.95	13.33	13.05	420	416
XV	3,5-Dinitrobenzoate	D	70	109-110	30.97	31.11	2.37	2.52	15.05	14.95		
XVI	4-Chloro-3-nitrobenzoate	D	22	112-113	31.70	31.46	2.42	2.75	12.32	11.95		
XVII	Benzenesulfonate	D	56	116-117	32.12	32.36	3.17	3.26	10.22	10.00	411	10,000
XVIII	<i>p</i> -Toluenesulfonate	D	66	97-100	33.88	33.90	3.53	3.63	9.88	9.71	425	10,000

^a These methods are given in the Experimental section.

bath there was added slowly 100 g. of propionyl chloride. A precipitate started to form during the addition of the acid chloride, and stirring was continued at 25° for 20 hours to complete the reaction. The mixture was washed several times with water and the organic material separated. Evaporation of the ether and recrystallization from hot ethanol of the crude product gave 110.2 g. (83.0%) of pentaerythritol propionate trinitrate, m.p. 38-40°. In some runs benzene was used as a solvent and in others no solvent was employed. This method was not generally applicable. For a number of the more difficultly esterified acids and for the dibasic acids, pyridine had to be used as a hydrohalogen acceptor. In the case of dibasic acid chlorides, the stoichiometric quantity of pentaerythritol trinitrate was employed to give the diester.

Method D.—To a solution of 10.5 g. of pentaerythritol trinitrate and 3.8 g. of phthalyl chloride in a three-necked flask in a water-bath there was added slowly with stirring 3.0 g. of pyridine. The mixture was heated for one hour at 50-70° and then washed with water and ethanol. Recrystallization of the solid from acetone-ethanol gave 8.4 g. (68%) of pentaerythritol phthalate trinitrate, m.p. 115-117°. For preparation of dibasic acid esters, the stoichiometric quantities of pentaerythritol trinitrate and the dibasic acid chloride were employed. Variations in concentration of the recrystallizing solvents in accord with ester solubility were necessary.

Method E.—To a solution of 9.0 g. of pentaerythritol trinitrate, 6.0 g. of benzoyl chloride and 20 g. of ether in a three-necked flask there was added a solution of 1.5 g. of sodium hydroxide in 10 g. of water. After stirring the reaction mixture for two hours at 25°, it was filtered and the solid precipitate combined with the organic layer. After evaporation of the ether from the combined crude product, the white solid was recrystallized from ethanol to give 7.3 g. (61%) of pentaerythritol benzoate trinitrate, m.p. 89-90°.

Method F.—To a mixture of 15 g. of pentaerythritol trinitrate and 10 g. of acetic anhydride at 25° with stirring there was added 1 g. of concentrated sulfuric acid. The white solid, that formed immediately, was washed with water and then recrystallized from hot ethanol to give 13.5 g. (78%) of pentaerythritol acetate trinitrate, m.p. 87-88°. The use of phosphoric acid instead of sulfuric acid gave the same results.

Method G.—To a mixture of 105 g. of pentaerythritol trinitrate and 55 g. of acetic anhydride at 25° there was added 43 g. of pyridine with cooling. After two hours the resultant mixture was washed with water and filtered. Recrystallization of the solid from hot ethanol gave 105 g.

(86.6%) of pentaerythritol acetate trinitrate, m.p. 87-88°.

Isolation of Pentaerythritol Tetranitrate from Esterification Reactions.—A mixture of 13.5 g. of pentaerythritol trinitrate and 20.0 g. of trichloroacetyl chloride was stirred for ten hours at 25°. The mixture was washed with water and the organic layer recrystallized from ethanol to give 0.7 g. (4%) of pentaerythritol tetranitrate, m.p. 135-138°, mixed m.p. 135-138°. A similar reaction with dichloroacetyl chloride gave a 4% yield of pentaerythritol tetranitrate.

A solution of 22 g. of pentaerythritol trinitrate, 9 g. of benzoic acid, 70 g. of benzene and 5 g. of sulfuric acid after standing for ninety minutes gave copious fumes of nitrogen oxides. The solution was added to water and filtered to give a precipitate which on recrystallization from acetone-ethanol gave 4.8 g. (20.6%) of pentaerythritol tetranitrate, m.p. 134-137°, mixed m.p. 135-138°. Repetition of this experiment with propionic acid gave an 11.5% yield of pentaerythritol tetranitrate.

The reaction of 3 g. of pentaerythritol trinitrate and 4 g. of concd. sulfuric acid at 25° for 20 minutes gave a white solid on dilution with water. Recrystallization of the white solid from acetone-ethanol-water gave a 10% yield of pentaerythritol tetranitrate, m.p. 138-140°, mixed m.p. 138-140°.

Neutral Equivalents of Esters of Pentaerythritol Trinitrate.—A 0.08 g.-0.25 g. sample of the compound was dissolved in acetone and to this was added a 100% molar excess of 0.1 *N* sodium hydroxide. After 30 minutes the solution was back-titrated to a phenolphthalein end-point to give the equivalents listed in Table I. Pentaerythritol trinitrate under these conditions gave a neutral equivalent of 26,000, and after 16 hours a neutral equivalent of 780 (theoretical for removal of one nitrate group 273).

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