2,2,2-Trinitroethyl Acetate.—To 14 g. of redistilled acetyl chloride in a round-bottom flask fitted with a condenser, there was added 6 g. of trinitroethanol in 10 cc. of ether. After removal of the ether by heating, an additional 7 g. of acetyl chloride was added. On heating at 100° copious fumes of hydrogen chloride were evolved. After two hours at 100° the reaction solution was cooled and added to water. The organic layer was separated and then distilled to give 5.5 g. of 2,2,2-trinitroethyl acetate, b. p. 118° (4 mm.), $n^{20}\text{D}$ 1.4478, d^{25} 1.474, 75% yield.

Anal. Calcd. for $C_4H_5N_3O_8$: C, 21.53; H, 2.26. Found: C, 21.30; H, 2.23.

2,2,2-Trinitroethyl Propionate.—The above experiment was repeated with the substitution of propionyl chloride for acetyl chloride. Quantities used were 4 g. of trinitroethanol and 20 g. of propionyl chloride. Final distillation gave 4.7 g. of 2,2,2-trinitroethyl propionate, b. p. 125° (6 mm.), $n^{25}\text{D}$ 1.4452, d^{25} 1.403, 90% yield.

Anal. Calcd. for $C_5H_7N_3O_8$: C, 25.32; H, 2.98. Found: C, 25.80; H, 3.32.

Reaction with Alkali.—Mixtures of weighed samples (0.3 g.) of the 2,2,2-trinitroethyl esters and a measured excess of 0.1 *N* aqueous sodium hydroxide were shaken until they became homogeneous (5 minutes). Back-titration with standard hydrochloric acid gave for the equivalent weight of 2,2,2-trinitroethyl acetate a value of 85.8 (calcd. for three equivalents per molecular weight, 77.4; for two equivalents, 111.6); for the equivalent weight of 2,2,2-trinitroethyl propionate, 90.2 (calcd. for three equivalents per molecular weight, 79.1; for two equivalents per molecular weight, 118.6). Trinitroethanol by direct titration with standard aqueous sodium hydroxide gave an equivalent weight of 182.6 (calcd. for one equivalent per molecular weight, 181.2). However, trinitroethanol on the addition of excess of sodium hydroxide and back-titration with hydrochloric acid gave an equivalent weight of 176 with a fading end-point. Use of 0.2 *N* alcoholic potassium hydroxide gave a neutral equivalent of 165 with a fading end-point.

Saponification equivalents for the above compounds were determined in the usual manner, using an excess of alcoholic potassium hydroxide, heating for 30 minutes, and back-titration with standard hydrochloric acid. Equivalent weights obtained were 77.0 for 2,2,2-trinitroethyl acetate (calcd. for three equivalents per molecular weight, 74.4); 81.7 for 2,2,2-trinitroethyl propionate (calcd. 79.1); and 95 to 134 for trinitroethanol (calcd. for two equivalents per molecular weight, 90.6).

Ionization Constant of Trinitroethanol.—The method used required that the sodium salt of the acid should be formed during the titration with sodium hydroxide. The formation of the sodium salt was indicated by the following experiment. To an aqueous solution of 1.5 g. of 2,2,2-trinitroethanol there was added 6 ml. of 5% aqueous sodium hydroxide. This solution was just basic to phenolphthalein. The mixture was reacidified with concentrated hydrochloric acid and extracted with ether. The ethereal extracts on distillation gave 1.3 g. of trinitroethanol, b. p. 108° (16 mm.), 87% recovery.[4]

Determination of the acid strength was made by a potentiometric method using a Coleman model 3 *p*H electrometer.[5] The ionization constant of benzoic acid determined by this method was 6.9×10^{-5} (lit. value 6.6×10^{-5}). The ionization constant determined for 2,2,2-trinitroethanol was $4.3 \pm 0.2 \times 10^{-3}$.

Acknowledgment.—Carbon and hydrogen analyses were performed by the Micro-Tech Laboratories, Skokie, Illinois.

DEPARTMENT OF CHEMISTRY
DE PAUL UNIVERSITY
CHICAGO 14, ILLINOIS
RECEIVED JUNE 14, 1950

---

[4] Use of a large excess of base and allowing the solution to stand for 72 hours before working up gave no recovery of trinitroethanol.

[5] For a recent application of this method see Newman, Taylor, Hodgson and Garrett, THIS JOURNAL, **69**, 1784 (1947).

2-Nitratoethyl Esters of Acrylic, Crotonic and Methacrylic Acids[1]

BY N. S. MARANS AND R. P. ZELINSKI

In continuation[2] of the investigation of nitrogen compounds containing acrylic, methacrylic or crotonic acid radicals we have synthesized 2-nitratoethyl acrylate, crotonate and methacrylate. These compounds were prepared by the reaction of 2-nitratoethanol with the corresponding acid chloride in the presence of cuprous chloride, a polymerization inhibitor. Both the 2-nitratoethyl acrylate and methacrylate were polymerized in the presence of benzoyl peroxide. 2-Nitratoethyl crotonate did not polymerize under the same conditions.

In aqueous sodium hydroxide at room temperature these esters reacted rapidly with an equivalent of base to yield 2-nitratoethanol and the sodium salt of the organic acid. In alcoholic potassium hydroxide they reacted with only about one-fifth of an equivalent. However, at reflux temperature in alcoholic potassium hydroxide, saponification was complete; *i. e.*, two equivalents of base were consumed.

Experimental

Acrylyl, methacrylyl and crotonyl chlorides were prepared by reaction of phosphorus trichloride[3] with the corresponding acids. The 2-nitratoethanol was prepared by the reaction of silver nitrate and ethylene chlorohydrin or bromohydrin.[4] The 2-nitratoethanol was purified by either distillation or fractionation, both under reduced pressure. In both cases the physical constants obtained were, b. p. 75° (5 mm.), $n^{25}\text{D}$ 1.4362, d^{25} 1.333.

2-Nitratoethyl Acrylate.—A mixture of 5.5 g. of 2-nitratoethanol, 16 g. of acrylyl chloride, and 1 g. of cuprous chloride was heated at 50° with considerable evolution of hydrogen chloride occurring. The mixture after having been washed with water was distilled to give 4.1 g. of 2-nitratoethyl acrylate, b. p. 100–103° (8 mm.), $n^{25}\text{D}$ 1.4500, d^{25} 1.246, 49% yield.

Anal. Calcd. for $C_5H_7NO_5$: C, 37.27; H, 4.38. Found: C, 36.87; H, 4.45.

2-Nitratoethyl Methacrylate.—A mixture of 10 g. of 2-nitratoethanol, 20 g. of methacrylyl chloride and 1 g. of cuprous chloride was heated at 50° for 30 minutes, and then was washed with 2% aqueous sodium hydroxide and finally with water. Distillation gave 8.7 g. of 2-nitratoethyl methacrylate, b. p. 90–95° (3 mm.), $n^{25}\text{D}$ 1.4518, d^{25} 1.207, 53% yield. Other attempts to purify this compound using fractionation in the presence of cuprous chloride gave extensive polymerization.

Anal. Calcd. for $C_6H_9NO_5$: C, 41.14; H, 5.18. Found: C, 40.50; H, 5.16.

2-Nitratoethyl Crotonate.—In the same manner a mixture of 9 g. of 2-nitratoethanol, 16 g. of crotonyl chloride and 1 g. of cuprous chloride yielded, after two distillations, 10 g. of 2-nitratoethyl crotonate, b. p. 122–125° (12 mm.), $n^{25}\text{D}$ 1.4580, d^{25} 1.191, 58% yield. In another preparation in which fractionation was used extensive decomposition of 2-nitratoethyl crotonate occurred.

---

[1] This work was performed with the aid of U. S. Navy funds under Subcontract number 2, Contract NOrd 9709 and Subcontract number 1, Contract NOrd 10431, both prime contracts being with the Hercules Powder Company, Allegany Ballistics Laboratory.

[2] N. S. Marans and R. P. Zelinski, THIS JOURNAL, **72**, 2125 (1950).

[3] Rehberg, Dixon and Fletcher, *ibid.*, **67**, 208 (1945).

[4] Henry, *Ann. chim.*, [4] **27**, 243 (1872).

Anal. Calcd. for $C_5H_9NO_5$: C, 41.14; sapn. equiv., 88.6. Found: C, 41.75; sapn. equiv., 86.8.

Polymerization of 2-Nitratoethyl Esters.—A 1-g. sample of 2-nitratoethyl methacrylate and 10 mg. of benzoyl peroxide on heating in a watch glass at 100° for twenty minutes gave a hard polymer. This compound also polymerized to a hard polymer after standing at 25° for a few days in the absence of a catalyst. 2-Nitratoethyl acrylate, 1 g., and 10 mg. of benzoyl peroxide on heating at 100° for one hour gave a soft, tacky polymer. The 2-nitratoethyl crotonate did not polymerize under these conditions.

Reaction with Alkali.—Mixtures of weighed samples of the 2-nitratoethyl esters (0.3 g.) and a measured excess of 0.1 *N* aqueous sodium hydroxide were shaken until they became homogeneous (5 minutes). Back-titration with standard hydrochloric acid gave for the equivalent weight for 2-nitratoethyl acrylate 164 (calcd. for one equivalent per molecular weight 161.2), for 2-nitratoethyl methacrylate 179 (calcd. 175.3), for 2-nitratoethyl crotonate 179 (calcd. 175.3) and for 2-nitratoethanol *ca.* 600 (calcd. 107.2).

The cleavage that occurred here was indicated to be that of the nitratoalkyl group from the unsaturated acid. A sample of 2.4 g. of 2-nitratoethyl crotonate was shaken with 2 g. of sodium hydroxide in 50 cc. of water until the mixture became homogeneous. Ethereal extracts of the solution on distillation gave 0.7 g. of 2-nitratoethanol, b. p. 95° (8 mm.), $n^{25}D$ 1.4366 and the saponification equivalent determined in the manner given below was 111 (calcd. 107).

Saponification equivalents for the three esters were determined in the following manner. A 0.3-g. sample was added to 25 ml. of 0.2 *N* alcoholic potassium hydroxide and the mixture refluxed for thirty minutes. Back-titration with standard acid gave the following equivalent weights: for 2-nitratoethyl acrylate, 80.5 (calcd. for two equivalents per molecular weight, 80.6), for 2-nitratoethyl methacrylate 88.4 (calcd. 88.5), for 2-nitratoethyl crotonate 86.8 (calcd. 88.5) and for 2-nitratoethanol 111 (calcd. 107).

A sample of 0.3 g. of 2-nitratoethyl crotonate was soluble on addition to 25 ml. of 0.2 *N* alcoholic potassium hydroxide. After standing for five minutes the solution was back-titrated with standard hydrochloric acid to give an equivalent weight of *ca.* 600. The experiment repeated with 2-nitratoethyl acrylate gave an equivalent weight of *ca.* 600.

Acknowledgment.—Carbon and hydrogen analyses were performed by the Micro-Tech Laboratories, Skokie, Illinois.

DEPARTMENT OF CHEMISTRY
DE PAUL UNIVERSITY
CHICAGO 14, ILLINOIS

RECEIVED JUNE 14, 1950

Some Properties of Pure γ-Butyrolactone

BY CLYDE MCKINLEY AND JOSEPH P. COPES

A highly purified sample of γ-butyrolactone has been prepared[1] and certain of its physical properties determined. Vapor pressures, using an isoteniscope, were determined and are presented in the table. Freezing point was determined using apparatus patterned after that in use by the National Bureau of Standards[2] and T_{f_0} was found to be $-43.53°$[3] by Mr. L. J. Lohr of this Laboratory. The refractive index, using an Abbe refractometer, was $n^{25}D$ 1.4348 and the density, using a pycnometer, was found as $d^{25}{}_4$ 1.1254.

P, mm.	Temp., °C.
50.1	119
79.4	132
125.9	145
199.6	159
316.3	174
501.2	189
708.0	201
760 (extrap.)	204 (extrap.)

GENERAL ANILINE AND FILM CORPORATION
CENTRAL RESEARCH LABORATORY
EASTON, PENNA.

RECEIVED JUNE 13, 1950

---

[1] For method see PB 60902.

[2] Research paper 1937.

[3] Calculations as in Bureau of Standards Technical Paper No. 1596, Research paper 1676.

Dipositive Silver as an Intermediate in Coulometric Analysis

BY DALE J. MEIER AND ERNEST H. SWIFT

Electrolytically generated bromine has been shown to be a satisfactory intermediate oxidant in coulometric titrations of arsenic(III), antimony(III) and thiodiglycol.[1] At the concentration of bromine and bromide ion existing in these titrations the use of bromine as the intermediate is limited by equilibrium considerations to the determination of reductants with half-cell potentials (Red. = Ox. + e^-) more positive than approximately -0.78 v. This value is obtained by assuming that the final approximate concentrations of bromide and tribromide were 10^{-1} and 10^{-6} *M*, respectively, and that the final ratio of $M_{ox.}$ to $M_{red.}$ was 1000. The negative limit of the oxidation potential can be extended somewhat by the use of chlorine as the intermediate, and Farrington and Swift[2] have described the use of chlorine for the determination of arsenic(III). In an effort to further extend the permissible negative limit of the half-cell potential of the reductant being determined, and also to find non-halide intermediates, we have investigated dipositive silver as an intermediate oxidant for coulometric titrations. The Ag(I)–Ag(II) formal potential has been determined by Noyes and his co-workers to be -1.98 v. in perchloric acid solutions.[3,4]

It has long been known that higher oxidation states of silver can be obtained by anodic oxidation, and although solid compounds can be precipitated which contain silver in a tripositive state, Noyes and his co-workers[5] have shown in

---

[1] R. Myers and E. H. Swift, THIS JOURNAL, **70**, 1047 (1948); R. A. Brown and E. H. Swift, *ibid.*, **71**, 2717 (1949); J. W. Sease, C. Niemann and E. H. Swift, *Ind. Eng. Chem., Anal. Ed.*, **19**, 197 (1947).

[2] P. S. Farrington and E. H. Swift, *Anal. Chem.*, **22**, 889 (1950).

[3] A. A. Noyes, D. DeVault, C. D. Coryell and T. J. Deahl, THIS JOURNAL, **59**, 1326 (1937).

[4] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 181.

[5] A. A. Noyes, J. L. Hoard and K. S. Pitzer, THIS JOURNAL, **57**, 1221 (1935); A. A. Noyes, K. S. Pitzer and C. L. Dunn, *ibid.*, **57**, 1229 (1935); A. A. Noyes and A. Kossiakoff, *ibid.*, **57**, 1238 (1935).