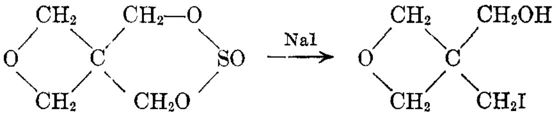
with sodium iodide during the reaction. The alkylation in the presence of water was found to cause the precipitation of sodium bisulfite instead and to increase the yield of 3-iodo-1-propanol in the reaction of trimethylene sulfite (I) with sodium iodide. A similar addition of water to a solution of pentaerythrityl disulfite and sodium iodide in methyl ethyl ketone was deleterious, as the alkylation reaction was slower and hydrolysis of the sulfite to pentaerythritol occurred.

The structure of 3-hydroxymethyl-3-iodomethyloxetane (IV) obtained from 2,4,8,3-trioxathiaspiro-[5,3]nonane-3-oxide (III)[3] was indicated by its elemental analysis and its infrared spectra.



III IV

The sulfite of 2-methyl-2-hydroxymethyl-1,3-propane-diol[3] required methyl isopropyl ketone as a solvent to effect a reaction. The reaction proceeded normally but the product, 2-methyl-2-hydroxymethyl-3-iodo-1-propanol was isolated as a 1:1 complex with 2-methyl-2-hydroxymethyl-1,3-propanediol. Dissociation of the complex occurs in acetone since after five crystallizations from this solvent 2-methyl-2-hydroxymethyl-1,3-propanediol could be obtained in pure condition.

The sulfite of 2,2-dimethyl-1,3-propanediol was resistant to alkylation and after refluxing with sodium iodide in methyl isopropyl ketone for forty-eight hours gave very little product. The stability of this cyclic sulfite is no doubt brought on by the *gem* methyl groups.

EXPERIMENTAL[4]

3-Iodo-1-propanol. A solution of 1,3,2-dioxanthiane-2-oxide[5] (24.4 g.), sodium iodide (30 g.), and water (3.6 g.) in methyl ethyl ketone (300 ml.) was refluxed for 24 hr. and formed a light yellow precipitate. The entire mixture was dried with anhydrous sodium sulfate and filtered. Fractional distillation under nitrogen gave 24.5 g. of 3-iodo-1-propanol boiling at 112° (31 mm.); n_{D}^{20} 1.5515; d_4^{25} 2.014. The literature[6] reports a boiling point of 115° (38 mm.) and a refractive index of n_{D}^{20} 1.5585.

Anal. Calcd. for C_3H_7OI: C, 19.38; H, 3.79. Found: C, 19.42; H, 3.58.

3-Hydroxymethyl-3-iodomethyloxetane (IV). 2,4,8,3-Trioxathiaspiro[5,3]nonane-3-oxide[3] (III) (10 g.) and sodium iodide (14.2 g.) were refluxed in methyl ethyl ketone for 20 hr. The solution was filtered, then acidified with dilute hydrochloric acid and separated from the water layer. Removal of the methyl ethyl ketone gave an oil which distilled at 128° (2 mm.); yield, 2.6 g.; n_{D}^{24} 1.5603.

Anal. Calcd. for $C_5H_9O_2I$: C, 26.31, H, 3.95. Found: C, 25.8; H, 3.80.

The infrared spectra of 3-hydroxymethyl-3-iodomethyloxetane had the characteristic oxetane absorption peak at 970 cm.$^{-1}$,[7] and hydroxyl peaks at 2850 and 3400 cm.$^{-1}$

2,2-Bisiodomethyl-1,3-propanediol. A mixture of sodium iodide (30 g.) and 2,4,8,10-tetraoxa-3,9-dithia[5,5]undecane-3,9-oxide[8] (22.8 g.) in dry methyl ethyl ketone (300 ml.) was refluxed for 36 hr. with constant stirring. Removal of the solvent gave a heavy oil which was extracted twice with methylene chloride (150 ml.). The solid which remained proved to be the starting material (2.7 g.).

The combined methylene chloride extracts were dried with calcium sulfate and upon removal of the solvent gave an oil (17 g.). Trituration with ethanol gave additional starting material (1 g.). Removal of the ethanol gave an oil which was crystallized from water and gave 2,2-bisiodomethyl-1,3-propanediol (11 g.) melting at 129–130°. The literature[9] reports a similar melting point.

Anal. Calcd. for $C_5H_{10}O_2I_2$: C, 16.86; H, 2.81. Found: C, 16.65; H, 3.02.

Reaction of sodium iodide with 5-methyl-5-hydroxymethyl-1,3,2-dioxathiane-2-oxide. A solution of sodium iodide (60 g.) and 5-methyl-5-hydroxymethyl-1,3,2-dioxathiane-2-oxide[3] (64 g.) in methyl isopropyl ketone (500 ml.) protected from light was refluxed with stirring for 48 hr. Removal of the solvent gave an oil which was separated by distillation into two fractions. The first fraction boiling at 110–140° (7 mm.) proved to be mainly starting materials (35 g.). The second fraction, which distilled at 160° (7 mm.), gave an oil which upon crystallization from chloroform gave 13.4 g. of a white solid melting at 70–71°. Analysis and a molecular weight determination in camphor indicated that this solid was a molecular complex of 2-methyl-2-hydroxymethyl-1,3-propanediol and 2-methyl-2-hydroxymethyl-3-iodo-1-propanol.

Anal. Calcd. for $C_{10}H_{22}O_5I$: C, 32.35; H, 6.76; I, 37.33. Found: C, 32.67; H, 6.58; I, 37.24. Mol. wt. 349.9. Found: 354.4, 350.8 (Rast) (Acetone, b.p. el.) 184, 145.

Five fractional crystallizations of the complex (3 g.) from acetone at −70° gave 0.05 g. of 2-methyl-2-hydroxymethyl-1,3-propanediol melting at 199–200°.

Reaction of 5,5-dimethyl-1,3,2-dioxathiane-2-oxide with sodium iodide. 5,5-Dimethyl-1,3,2-dioxathiane-2-oxide[10] (30 g.) and sodium iodide (30 g.) were refluxed in methyl isopropyl ketone (600 ml.) with stirring and protected against light for 48 hr. Removal of the solvent gave a dark residue which was fractionally distilled. Starting material (17.6 g.) was obtained together with 2.0 g. of a liquid which boiled at 106–110° (35 mm.). Two further distillations gave a sample which had an approximate analysis for 2,2-dimethyl-3-iodo-1-propanol.

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[3] S. Wawzonek and J. T. Loft, *J. Org. Chem.*, **24**, 641 (1959).

[4] Melting points and boiling points are not corrected.

[5] P. B. D. de la Mare, W. Klyne, D. J. Miller, J. G. Pritchard, and D. Watson, *J. Chem. Soc.*, 1813 (1956).

[6] J. P. Henry, *Chem. Z.*, **1897**, II, 344.

[7] S. Searles, *J. Am. Chem. Soc.*, **75**, 1175 (1953); J. W. Campbell, *J. Org. Chem.*, **22**, 1029 (1957).

[8] L. Orthner, *Ber.*, **61B**, 116 (1928).

[9] H. Bincer and K. Hess, *Ber.*, **61B**, 537 (1928).

[10] D. G. Markees and A. Burger, *J. Am. Chem. Soc.*, **71**, 2031 (1949).

Preparation of 2,2,2-Trinitroethanol[1]

HENRY FEUER AND THOMAS J. KUCERA

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The synthesis of trinitroethanol (I) has been reported from the reaction of trinitromethane with

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[1] From the Ph.D. Thesis of Thomas J. Kucera, Purdue University, August 1953.

an excess of paraformaldehyde.[2] The experimental procedure involved distillation of I and the authors reported that explosions were encountered during this operation. In addition, compound I made by this method was very low melting (30°) and unstable.

An investigation of this reaction in this laboratory by G. Leston[3] showed that compound I could be obtained with a much higher melting point (65–66°), but that it was still hygroscopic and decomposed in the presence of moisture.

We now wish to report a more efficient preparation of I which eliminates the explosion hazard and affords in 80% yield pure I, m.p. 72°, directly from the reaction solution.

Pure I was found to be nonhygroscopic and stable. The presence of small amounts of water and formaldehyde was found to decrease the melting point and to cause I to react with the absorbed atmospheric moisture. The ready dissociation of I to trinitromethane and formaldehyde in water has recently been studied.[4]

EXPERIMENTAL

2,2,2-Trinitroethanol. In a three-necked flask which was provided with a stirrer, reflux condenser, and thermometer were placed 100 ml. of carbon tetrachloride, 2.12 g. (1.4 mmoles) of trinitromethane and 0.45 g. of paraformaldehyde (14.3 mmoles of formaldehyde assuming 95% formaldehyde). The turbid solution was heated with stirring for 3 hr. at 60–65° and then at reflux for 30 min. Concentrating the solution to 30 ml. and cooling in the refrigerator gave trinitroethanol in the form of long needles. Further concentration of the filtrate gave additional crops of crystals, m.p. 72°. The overall yield was 80%.

Anal. Calcd. for $C_2H_3O_7N_3$: C, 13.26; H, 1.66; N, 23.20. Found: C, 13.22; H, 1.62; N, 23.02.

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[2] N. S. Marans and R. P. Zelinski, *J. Am. Chem. Soc.*, **72**, 5329 (1950).

[3] Unpublished results from the M.S. dissertation of G. Leston, Purdue, 1949.

[4] J. Reinhart, J. G. Meitner, and R. W. Van Dolah, *J. Am. Chem. Soc.*, **77**, 496 (1955).

Polymerizable Esters of Trinitroethanol[1]

Henry Feuer, Henry B. Hass, and R. D. Lowrey

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The preparation of polymerizable mononitroalcohol esters of acrylic acid was described by D'Alelio.[2] Marans and Zelinski[3] showed that trinitroethanol (I) reacts readily with acetyl chloride and propionyl chloride to give the expected esters of I in high yields. We now wish to report the preparation of esters of I with unsaturated acids which are enumerated in Table I. In all cases the acid chlorides were employed and with the monobasic acids the highest yields were obtained in the absence of a solvent. This was also the case with fumaryl chloride, but the reaction temperature had to be raised to 130°. In the preparation of ditrinitroethyl itaconate the reaction was performed in petroleum ether. On heating, trinitroethyl acrylate and trinitroethyl methacrylate (II) were converted to high melting translucent solids of high softening range. Ester II was also copolymerized with ditrinitroethyl fumarate.

Attempts to prepare a monomer from isopropenyl isocyanate and compound I were unsuccessful. Reactions which were carried out in the presence of a polymerization inhibitor such as trinitrobenzene led to a viscous oil which turned to a solid during distillation at low pressure. It had the correct analysis for a polymer of trinitroethyl *N*-isopropenylcarbamate.

EXPERIMENTAL

Trinitroethyl methacrylate (II). Three grams (0.019 mole) of trinitroethanol and 10 ml. of methacrylyl chloride were agitated with a stream of dry nitrogen while the temperature was raised to 80° and kept there for 3 hr. The excess acid chloride was removed *in vacuo*, the residue dissolved in ether, washed successively with water, 1.5*N* potassium carbonate, and again with water, and the ether solution was dried with calcium sulfate. Distillation at 95° and 5 mm. caused the ester to crystallize in the condenser. Recrystallization from petroleum ether (b.p. 60–70°) at −60° gave *trinitroethyl methacrylate*, m.p. 26°.

Trinitroethyl acrylate. The procedure was the same as described above, except that the reaction was carried out at 28° for 2 hr.

Ditrinitroethyl fumarate. The reaction was conducted at 100° for 4 hr. and then at 130° for 3 more hr. After work-up as described above, a solid, m.p. 119°, remained. It was recrystallized from dibutyl ether to give *ditrinitroethyl fumarate*, m.p. 150°.

Ditrinitroethyl itaconate. The procedure was the same as described for the preparation of ester II except that petroleum ether (b.p. 60–70°) was employed as a solvent and the reaction mixture was refluxed for 16 hr. Removal of the solvent gave an oil which solidified on adding ethanol. Recrystallization from ethanol gave *ditrinitroethyl itaconate*, m.p. 97°.

Polymerization experiments. Heating ester II at 70° in an airtight flask for 6 days gave a yellow translucent solid which softened at 250–280°.

Similar treatment of trinitroethyl acrylate gave a solid of softening range 170–210°.

Heating an equimolar mixture consisting of ester II and ditrinitroethyl fumarate in a sealed flask at 70° for 6 days gave a translucent solid softening at 150–190°.

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[1] From the Ph.D. Thesis of Robert D. Lowrey, Purdue University, February 1950.

[2] G. F. D'Alelio, U. S. Patent **2,499,804** (Sept. 21, 1948).

[3] N. S. Marans and R. P. Zelinski, *J. Am. Chem. Soc*. **72**, 5329 (1950).