the experiments carried out over long periods of time was valid, the water-soluble products from a sulfonation mixture kept at 2° for fifty hours prior to hydrolysis were partially separated by the fractional crystallization technique described above. The formation of 2-phenyl-2-hydroxy-1-ethanesulfonic acid and 2-phenylethene-1-sulfonic acid as the principal products was confirmed.

Sodium 1-Bromo-2-phenylethene-1-sulfonate.—A solution of 1.05 g. (0.005 mole) of sodium 2-phenylethene-1-sulfonate was treated with bromine water until a permanent yellow color remained. The solution was evaporated to dryness on a steam-bath with the aid of a current of air. The residue, after crystallization from 90% alcohol, weighed 1.20 g. (87%).

Anal. Calcd. for $C_8H_6O_3SBrNa$: Na, 8.07; Br, 28.03. Found: Na, 8.13; Br, 27.33.

A portion was converted to the sulfonamide (m. p. 130–131°) by the procedure used by Truce,[10] and this showed no depression in melting point when mixed with a sample of his 1-bromo-2-phenylethene-1-sulfonamide, m. p. 130–131°.

1,2-Dibromo-2-phenyl-1-ethanesulfonamide.—A solution of 1.0 g. of 2-phenylethene-1-sulfonamide[4] in about 50 ml. of acetic acid was treated with an equimolar quantity of bromine, and the solution kept in sunlight for three hours. Oxygen appears to catalyze the reaction since decolorization occurs first at the surface. Concentration of the acetic acid at room temperature to about 15 ml. gave 1.0 g. (55%) of crystalline material. After two crystallizations from benzene, colorless needles, m. p. 161–162°, were obtained.

Anal. Calcd. for $C_8H_9O_2Br_2NS$: C, 27.96; H, 2.73. Found: C, 28.00; H, 2.79.

Triethylammonium bromide precipitated immediately when 0.1 g. of 1,2-dibromo-2-phenyl-1-ethanesulfonamide in a warm benzene solution was treated with excess triethylamine. Evaporation of the benzene and crystallization from water gave 1-bromo-2-phenylethene-1-sulfonamide.[10]

Sulfonation of Styrene at 54.4°.—Dioxane sulfotrioxide was prepared from 76.1 g. (0.951 mole) of sulfur trioxide, 83.7 g. (0.951 mole) of dioxane and 150 ml. of dry ethylene dichloride. A solution of 99.0 g. (0.951 mole) of styrene in 30 ml. of ethylene dichloride was added to this reagent in the course of two and one-third hours, the temperature being maintained at 5–7°. After an additional fifteen minutes at 10° two aliquots were withdrawn (by means of a 10-ml. pipet), weighed and hydrolyzed. The remaining solution was heated on the steam-bath to 55° as rapidly as possible, whereupon it was placed in a thermostat at 54.4°. Further aliquots were withdrawn at intervals. The fraction of sulfur trioxide present in each aliquot was determined from the weight of the reaction mixture and the weight of the aliquot. The aliquots were quenched immediately in ice-water, the weight of the aliquot being determined by the increase in weight of the flask holding the ice-water. Ether was added to each aliquot and the layers separated, using sodium chloride to break emulsions where necessary. After washing thoroughly the organic layer was dried and evaporated to dryness at room temperature, the weight of the residue being taken as an approximation of the quantity of 2,4-diphenyl-1,4-butanesultone[8] (III). The water layer was titrated (to phenolphthalein) with standard sodium hydroxide, then acidified and treated with 0.1 mole of barium chloride per mole of sulfur trioxide in the aliquot. The barium sulfate was determined gravimetrically (analysis reproducible to within 1% of the total sulfur trioxide). The filtrate was titrated by the bromate–bromide method to determine the amount of sodium 2-phenylethene-1-sulfonate present. The results are summarized in Table II.

Summary

1. Sulfonation of styrene at temperatures below 5° gave (after hydrolysis and neutralization) sodium 2-hydroxy-2-phenyl-1-ethanesulfonate (II) as the major product. β-Phenylethionic anhydride was ruled out as the principal precursor of II.

2. Titration with aqueous bromine using the bromate–bromide method was used to determine sodium 2-phenylethene-1-sulfonate (I) in the presence of II. A mechanism is given for the rapid reaction of I with bromine in aqueous solution.

3. The olefin–sulfur trioxide intermediate complex previously postulated[2] was useful in accounting for the various products formed in the sulfonation of styrene.

EVANSTON, ILLINOIS RECEIVED MARCH 29, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Formation of Ethers in the Preparation of Pentaerythritol

BY STANLEY WAWZONEK AND DONALD A. REES[1,2]

The preparation of pentaerythritol from acetaldehyde and formaldehyde is always accompanied by the formation of dipentaerythrityl ether.[3]

Attempts[3] to arrive at a mechanism by increasing the amount of dipentaerythrityl ether formed in this condensation proved unsuccessful. The only conclusion made was that pentaerythritol was not necessary for the formation of dipentaerythrityl ether.

One possible mechanism for the formation of dipentaerythrityl ether is outlined in the following series of reactions

$$\mathrm{CH_3CHO + HCHO \overset{OH^-}{\rightleftharpoons} CH_2OHCH_2CHO} \quad (1)$$

$$\mathrm{CH_2OHCH_2CHO \rightleftharpoons CH_2{=}CHCHO + H_2O} \quad (2)$$

$$\mathrm{CH_2{=}CH{-}CHO + HOCH_2CH_2CHO \rightleftharpoons O(CH_2CH_2CHO)_2} \quad (3)$$

$$\mathrm{O(CH_2CH_2CHO)_2 + 6HCHO + 2OH^- \longrightarrow O(CH_2C(CH_2OH)_3)_2 + 2HCOO^-} \quad (4)$$

The existence of an equilibrium between acrolein and β-hydroxypropionaldehyde in aqueous and acid solutions has already been demonstrated by Lucas.[4] Addition of an alcohol to acrolein in

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(1) A. C. S. Pre-Doctoral Fellow, 1946–1947.

(2) Abstracted from a thesis by Donald A. Rees, submitted to the Graduate Faculty of the State University of Iowa in partial fulfilment of the requirements for the degree of Doctor of Philosophy, August, 1947.

(3) Friederick and Brun, *Ber.*, **63**, 2681 (1930).

(4) Lucas and Pressman, THIS JOURNAL, **64**, 1953 (1942).

the presence of alkali is the subject of a patent.[5]

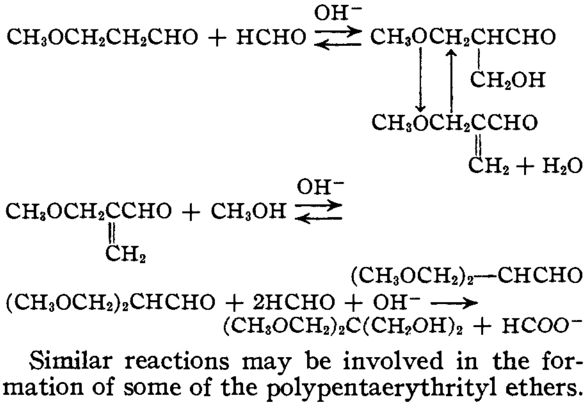
In the present investigation evidence has been obtained for the formation of ethers of pentaerythritol, by the reactions cited above, in the Tollens condensation.

The formation of pentaerythritol under the usual conditions[6] in an aqueous solution containing 50% methanol by volume gave a product which, to aid separation, was propionated. The mixture of propionates obtained was separated by distillation into pentaerythrityl tetrapropionate, the tripropionate of methylpentaerythrityl ether, and the dipropionate of dimethylpentaerythrityl ether. Identification was accomplished by saponification to pentaerythritol, methylpentaerythrityl ether and dimethylpentaerythrityl ether.

Methylpentaerythrityl ether and dimethylpentaerythrityl ether were also separated by chromatographic adsorption of their *p*-phenylazobenzoates.

The formation of methylpentaerythrityl ether indicates that acrolein is an intermediate in the formation of pentaerythritol and that it can add alcohols that may be present to form ethers. The ethers on further reaction with formaldehyde give ethers of pentaerythritol. In the present investigation methyl alcohol gave methylpentaerythrityl ether. Under the usual conditions[6] for preparing pentaerythritol, β-hydroxypropionaldehyde or products resulting from the reaction of β-hydroxypropionaldehyde and formaldehyde or even pentaerythritol can add to acrolein and give rise to dipentaerythrityl ether. The reaction of the last two with more than one molecule of acrolein would give rise to the polypentaerythrityl ethers mentioned in the patent literature.

The formation of dimethylpentaerythrityl ether is entirely consistent with the mechanism proposed. Its formation could proceed from β-methoxypropionaldehyde.



$$CH_3OCH_2CH_2CHO + HCHO \overset{OH^-}{\rightleftharpoons} CH_3OCH_2\underset{\displaystyle CH_2OH}{\underset{|}{C}}HCHO \;\; \downarrow\uparrow \;\; CH_3OCH_2\underset{\displaystyle CH_2}{\underset{\|}{C}}CHO + H_2O$$

$$CH_3OCH_2\underset{\displaystyle CH_2}{\underset{\|}{C}}CHO + CH_3OH \overset{OH^-}{\rightleftharpoons} (CH_3OCH_2)_2\text{—}CHCHO$$

$$(CH_3OCH_2)_2CHCHO + 2HCHO + OH^- \longrightarrow (CH_3OCH_2)_2C(CH_2OH)_2 + HCOO^-$$

Similar reactions may be involved in the formation of some of the polypentaerythrityl ethers.

Experimental[7]

Preparation of Pentaerythritol in 50% Methanol.—To a suspension of paraformaldehyde (240 g.) in water (750 ml.) and methanol (750 ml.) containing 63 g. of acetaldehyde, there was added 53 g. of powdered quicklime in rather large portions at first in order to bring the temperature to 45° and then at a rate to maintain the temperature between 50–55°. The mixture became slightly yellow in color. After the addition was complete, stirring was continued for an additional three hours. To the resulting mixture, oxalic acid (141 g.) was added; the solid was removed by filtration and washed with two 500-ml. portions of water. The combined filtrates were evaporated under reduced pressure to dryness. The last traces of water were removed by adding 200 ml. of propionic acid and repeating the distillation under reduced pressure. The product obtained was a dark brown sirup.

Separation of the Products.—To a mixture of the sirup and propionic anhydride (780 ml.) at 0°, concentrated sulfuric acid (30 ml.) was added dropwise keeping the temperature below 4°. The resulting solution was stirred overnight at room temperature and then at 100° until solution of the sirup was complete. After two more hours at this temperature, the solution was heated under reduced pressure to remove the excess propionic anhydride, and the propionic acid formed. The liquid obtained was cooled, poured onto ice (1500 g.) and neutralized with sodium bicarbonate. Extraction with ether gave 287 g. of a deep brown colored sirup which was first rapidly distilled at 0.1 mm. from a Claisen flask. A second distillation at 4 mm. through a Vigreux column gave three distinct fractions.

Fraction	Yield, g.	B. p., °C.
I	14.5	135–148
II	52.0	165–172
III	167.4	172–197

Fraction I upon refractionation gave the dipropionate of dimethylpentaerythrityl ether, b. p. 135–138° at 6 mm., n^{25}_D 1.4361, d^{20} 1.057.

Anal. Calcd. for $C_{\,3}H_{24}O_6$: C, 56.50; H, 8.75; OCH_3, 22.46. Found: C, 56.62; H, 8.67; OCH_3, 20.41.

The dipropionate of dimethylpentaerythrityl ether (5.4 g.) was refluxed with a slight excess of sodium methoxide in methanol (20 ml.) for two hours. The resulting solution was neutralized with dilute hydrochloric acid and evaporated to dryness. Extraction with chloroform gave an oil which was recrystallized from (60–70°) petroleum ether; m. p. 34–35°; yield 0.5 g. A mixture with an authentic sample[8] melted at the same temperature.

Fraction II upon refractionation gave the tripropionate of methylpentaerythrityl ether, b. p. 170–172° at 5–6 mm., n^{25}_D 1.4410, d^{20} 1.081.

Anal. Calcd. for $C_{15}H_{26}O_7$: C, 56.59; H, 8.23; OCH_3, 9.75. Found: C, 56.79; H, 8.18; OCH_3, 9.03.

The tripropionate of methylpentaerythrityl ether (17 g.) was saponified in a similar manner to that used for the dipropionate of dimethylpentaerythrityl ether. The oil obtained was crystallized from chloroform; m. p. 65–67°; yield 2.3 g. A distillation at reduced pressure (2 mm.) followed by a crystallization from chloroform gave white crystals melting at 71–72°. A mixture with an authentic sample[8] melted at the same temperature.

Fraction III upon refractionation gave pentaerythrityl tetrapropionate, b. p. 184–186° at 3 mm.; m. p. 35–37°. This compound is reported in the patent literature[9] as a liquid.

Anal. Calcd. for $C_{17}H_{28}O_8$: C, 56.65; H, 7.83. Found: C, 56.45; H, 7.81.

Pentaerythrityl tetrapropionate (5.0 g.) was saponified by refluxing with sodium methoxide (0.02 g. of sodium) in dry methanol (50 ml.). Completion of the reaction was indicated by complete solution of a few drops of the reaction mixture in water. Upon cooling pentaerythritol

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[5] Heyse, German Patent 554,946 [*C. A.*, **26**, 5964 (193[illegible])].

[6] Schurink, "Organic Syntheses," Coll. Vol. I, 425 (1941).

[7] Melting points are corrected while boiling points are not.

[8] Orthner and Freyss, *Ann.*, **484**, 131 (1930).

[9] Holt, U. S. 2,031,603; *C. A.*, **30**, 2200 (1936).

crystallized from the reaction mixture. One crystallization from water gave a product (1.5 g.) melting at 259°.

Deacylation and Chromatographic Separation of Fraction I.—Fraction I (3 g.) was deacylated in a similar fashion to that used for pentaerythrityl tetrapropionate. Removal of the methanol gave a sirup which was treated in dry pyridine (50 ml.) and *p*-phenylazobenzoyl chloride[10] (3 g.). The mixture was shaken for a short time and then heated at 85° for three days. The resulting solution was shaken with water (2 ml.) for fifteen minutes and then poured onto ice (300 g.) with vigorous stirring. The resulting mixture was neutralized with sodium bicarbonate and extracted repeatedly with chloroform. The combined chloroform extracts were washed once with water and dried. Chromatographic separation was performed on a column of silicic acid 60 cm. long and 3.3 cm. in diameter. Two distinct bands were obtained. Using chloroform as the eluent, the lower band of the tri-*p*-phenylazobenzoate of methylpentaerythrityl ether was run completely through the column in order to separate the di-*p*-phenylazobenzoate of dimethylpentaerythrityl ether from the *p*-phenylazobenzoic acid. The chloroform solution of the tri-*p*-phenylazobenzoate of methylpentaerythrityl ether was concentrated to 55 ml., mixed well with ethanol (100 ml.) and allowed to stand at 0° until no more precipitate formed. The light orange crystals were filtered, washed with ethanol and recrystallized from ligroin, m. p. 190–191°.

Anal. Calcd. for $C_{45}H_{38}N_6O_7$: C, 69.77; H, 4.95; azoyl, 81.0; mol. wt., 774. Found: C, 70.08; H, 4.87; azoyl, 80.4; mol. wt. (Rast), 773, 793.

The di-*p*-phenylazobenzoate of dimethylpentaerythrityl ether was separated mechanically and removed from the silicic acid with a mixture of chloroform and ethanol. Removal of the solvent gave an orange solid which was recrystallized from ligroin, m. p. 93–94°.

Anal. Calcd. for $C_{33}H_{32}O_6N_4$: C, 68.27; H, 5.51; Found: C, 67.50; H, 5.25.

Summary

The Tollens condensation of acetaldehyde with formaldehyde in 50% methanol gives a mixture of pentaerythritol, methylpentaerythrityl ether and dimethylpentaerythrityl ether.

A mechanism for the formation of ethers in the preparation of pentaerythritol is proposed.

IOWA CITY, IOWA

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(10) Coleman, Nichols, McCloskey and Auspon, "Organic Syntheses," **25**, 87 (1945).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Oxidations of Certain Polyacetyl-β-D-thioglycosides to the Corresponding Sulfones

BY WILLIAM A. BONNER AND RICHARD W. DRISKO

A single paper by Wrede and Zimmermann[1] seems to be the only report to date considering the oxidation of carbohydrate derivatives containing divalent sulfur. These investigators prepared di-tetraacetylglucosyl sulfone, di-tetraacetylgalactosyl sulfone, di-heptaacetylcellobiosyl sulfone and methyl 6-sulfo-bis-(6-desoxy-2,3,4-triacetyl-β-D-glucoside) by oxidation of the corresponding sulfides with potassium permanganate in acetic acid. Treatment of the first three of these compounds with ammonia in methanol led to the corresponding deacetylated substances. Since the chemistry of the sulfone derivatives in the sugar series has received little attention, and since no sulfones related to the simple thioglucosides have been prepared, it seemed desirable to prepare and study a few representative members of this class of compounds.

When phenyl tetraacetyl-β-D-thioglucoside was dissolved in acetic acid and treated with a slight excess of aqueous potassium permanganate, phenyl tetraacetyl-β-D-glucosyl sulfone resulted in excellent yield and purity. Phenyl triacetyl-β-D-xylosyl, phenyl triacetyl-D-arabinosyl, and ethyl tetraacetyl-β-D-glucosyl sulfones were similarly prepared. Hydrogen peroxide in acetic acid, after the method of Gilman and Beaber,[2] was also found effective in oxidizing thioglycosides to the corresponding sulfones. Phenyl, benzyl and ethyl tetraacetyl-β-D-glucosyl sulfones were prepared in good yield in this manner. It is noteworthy that when hydrogen peroxide was used as oxidant, the oxidation process was apparently attended by deacetylation of the acetylated thioglucoside despite the acetic acid solvent. This unexpected phenomenon is under further investigation at the present time.

The alkyl and aryl polyacetyl-β-D-glycosyl sulfones prepared in this study were white, nicely crystalline substances. The physical properties of the sulfones prepared in this study are contrasted with those of the corresponding parent polyacetyl-β-D-thioglycosides in Table I. It is seen that oxidation of the divalent sulfur atom in the acetylated thioglycoside to the sulfone state brings about the substantial melting point increase usually observed in converting a thioether to its sulfone.[3] Accurate correlations of the trends in the change of optical activity accompanying oxidation of the thioglycoside to its sulfone cannot be made on the basis of the data at hand, but it is apparent from Table I that such changes in rotatory power probably depend both upon the nature of the thio-aglucone and the configuration of the glycosyl residue.

By use of the calculated quantity of potassium permanganate as oxidant an attempt has been made to convert phenyl tetraacetyl-β-D-thioglucoside into phenyl tetraacetyl-β-D-glucosyl sulfoxide, a typical representative of the class intermediate

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(1) Wrede and Zimmermann, *Z. physiol. Chem.*, **148**, 65 (1925).

(2) Gilman and Beaber, THIS JOURNAL, **47**, 1449 (1925).

(3) *Cf.* C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 661 ff.