

THE REACTION
OF
3,3 bis(HYDROXYMETHYL)-OXACYCLOBUTANE
WITH
SOME PRIMARY ALCOHOLS

BY

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submitted in partial fulfillment for the requirements
of the degree Master of Science
in the Chemistry Department of the
American University of Beirut
Beirut, Lebanon
June 1955

ETHERS OF PENTAERYTHRITOL

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ACKNOWLEDGMENT

The author wishes to express her gratitude to the Research Corporation for a Fellowship that made this work possible.

The author also wishes to thank Professor C.H. Issidorides who suggested this problem and encouraged it with steady interest and council.

ABSTRACT

Monomethyl pentaerythrityl ether was prepared in 82% yield by the reaction of 3,3 bis-(hydroxymethyl)-oxacyclobutane with methyl alcohol in the presence of catalytic amounts of sulfuric acid. The action on this compound of acetic anhydride and of triphenylchloromethane gave the corresponding triacetate and tritryl derivatives.

The reaction of ethyl alcohol with 3,3 bis-(hydroxymethyl)-oxacyclobutane in the presence of catalytic amounts of sulfuric acid or p-toluene sulfonic acid gave 2.7 - 33% yield of monoethyl pentaerythrityl ether together with some polymeric side-products. A similar procedure using n-propyl alcohol failed to give any definite products.

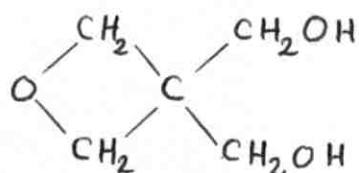
During the preparation of 3,3 bis-(hydroxymethyl)-oxacyclobutane from monobromopentaerythritol and alcoholic potassium hydroxide, an unsaturated side-product was isolated. It was identified as 1,3 propanediol,2 methylene by conversion to its diacetate and dichloride.

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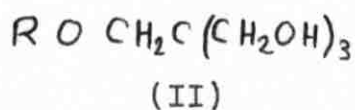
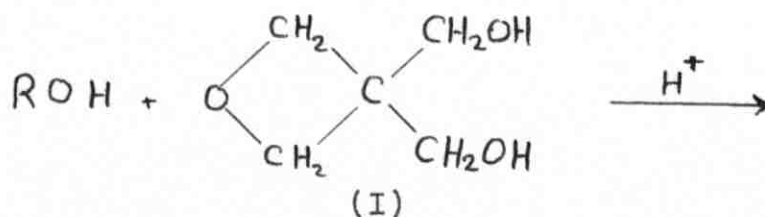
INTRODUCTION

The reactions of 1,2 epoxides with many reagents such as alcohols, phenols, amines and organometallic compounds have been well established and systematically studied¹. However, very little work has been done on the corresponding reactions of 1,3 epoxides. This is especially true of substituted trimethylene oxides such as 3,3 bis(hydroxymethyl)-oxacyclobutane (I):



(I)

The purpose of this research was to study the feasibility of an acid-catalyzed reaction between (I) and primary alcohols to give the corresponding monoalkyl ethers of pentaerythritol (II):

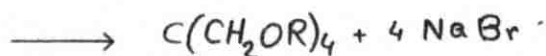
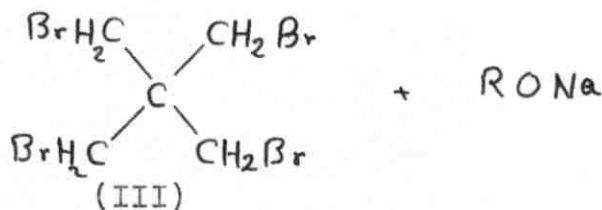


Compounds of the type (II) are polyhydroxy analogs of the cellosolves. According to the patent literature^{2,3}, some of these ether-alcohols of pentaerythritol are used as plasticizers and emulsifiers or as intermediates in the preparation of pharmaceutical products.

HISTORICAL

A survey of the literature indicates that many ethers of pentaerythritol have been synthesized by a variety of methods. The reactions used are, in some cases, not clean cut and often give a mixture of products.

Pentaerythrityl tetrabromide (III) has been used as the starting material for the preparation of many tetraethers (IV) of pentaerythritol with alcohols and phenols, by a direct application of the Williamson synthesis⁴:

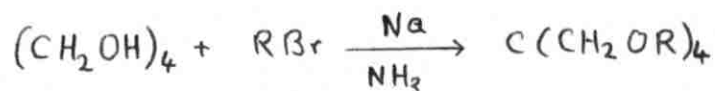


(IV)

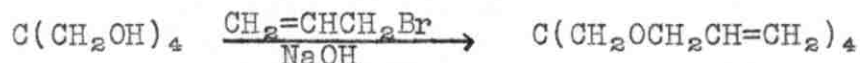
However, the reaction proceeds satisfactorily only when the reactants are heated in sealed tubes for prolonged periods of time. The low reactivity of pentaerythrityl tetrabromide in bimolecular reactions of this type has been ascribed to its neopentyl structure⁵.

Treatment of the sodium salt of pentaerythritol

in liquid ammonia with an alkyl bromide gives the corresponding tetraethers as the main product together with some tri- and diethers⁶:



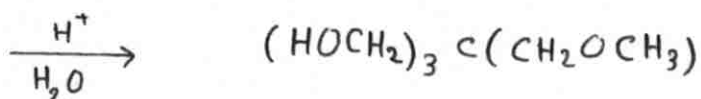
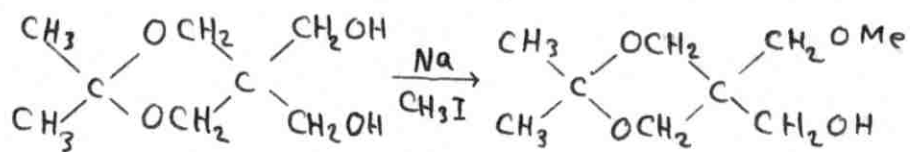
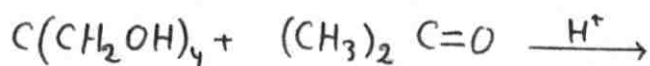
When a reactive halide is used, ether formation can be carried out by treating pentaerythritol with the halide in the presence of alkali. The allyl ethers of pentaerythritol have been prepared in this way^{7,8}. By varying the amounts of alkali and allyl bromide, the tri- or tetraethers can be made to predominate:



A special class of ethers of pentaerythritol has attracted considerable attention recently. This consists of compounds of the cellosolve type obtained from the reaction of pentaerythritol with a 1,2 epoxide in the presence of certain catalysts. The oily products formed are claimed to be useful solvents and plasticizers for many substances such as cellulose ethers, cellulose nitrate and phenol-aldehyde resins. The preparation of these pentaerythritol ethers has been the subject of several patents^{2,3,9}.

In order to obtain the mono- and diethers of

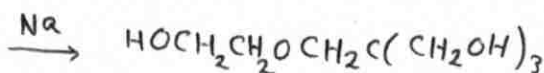
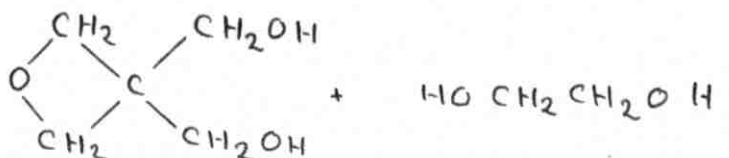
pentaerythritol Orthner and Freyss¹⁰ blocked two alcohol functions of pentaerythritol by ketal formation with acetone and treated the resulting monoisopropylidene derivative with methyl iodide in the presence of sodium. The yields, however, were very low:



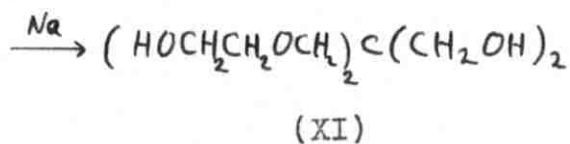
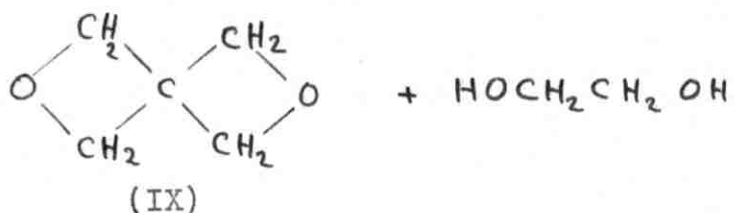
An entirely novel method for the preparation of monoalkyl and dialkyl ethers of pentaerythritol was introduced by Wawzonek and Rees¹¹, who prepared the monomethyl and dimethyl ethers of pentaerythritol by running the Tollens condensation of acetaldehyde and formaldehyde in 50% aqueous methanol. In the course of this reaction methyl alcohol adds to the acrolein intermediate (V) to give β -methoxypropionaldehyde (VI) which then condenses

relatively impure and difficult to isolate. The mono-methyl ether has also been prepared in poor yield by the addition of methanol to acrolein, followed by treatment of the resulting β -methoxypropionaldehyde with formaldehyde¹³. A similar method has been used in Germany for the preparation of other monoalkyl ethers of pentaerythritol¹⁴. The preparation of pentaerythrityl monomethyl ether from formaldehyde and acetaldehyde in the presence of methyl alcohol and potassium hydroxide is the subject of a very recent patent¹⁵. The compound, however, is reported to melt over a wide range (60 - 67°) and is probably impure.

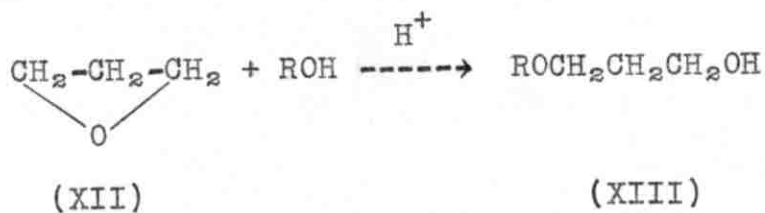
The first examples reported in the literature of the opening of trimethylene oxide rings with alcohols were the reactions of 3,3 bis(hydroxymethyl) oxacyclobutane (I) and 2,6-dioxaspiro (3,3) heptane (IX) with the sodium salt of ethylene glycol to give the monoethylene glycol ether (X) and the bis-(ethylene glycol) ether (XI) of pentaerythritol¹².



(X)

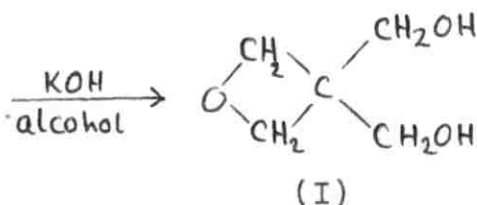
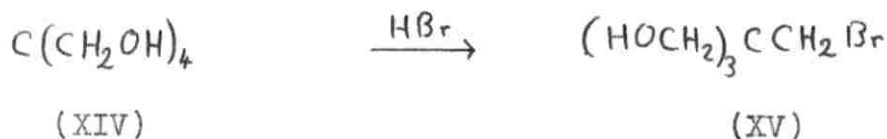


While the present work was in progress, Searles and Butler¹⁶ reported the reaction of trimethylene oxide (XII) with alcohols in the presence of acids or alkoxides to give the corresponding ethers of trimethylene glycol (XIII), in moderately good yields.



RESULTS

The starting material, 3,3 bis(hydroxymethyl)-oxa-cyclobutane (I), was prepared from pentaerythritol by the following sequence of reactions:



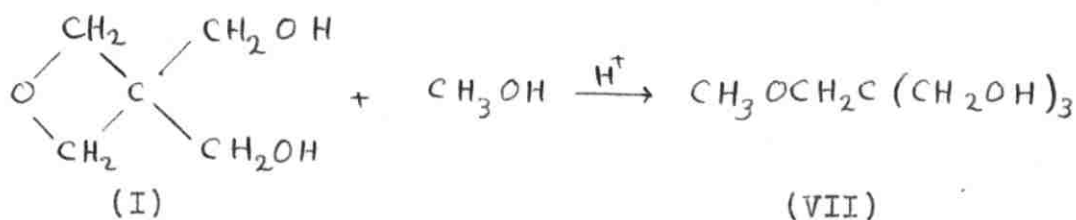
Pentaerythrityl monobromide (XV) was prepared by the action of 48% hydrobromic acid on pentaerythritol in glacial acetic acid, followed by transesterification of the bromoacetates and exhaustive extraction of the crude product with dry ether. The monobromide, after recrystallization, melted at 75 - 76°. This method is a modification of the procedure of Beyaert and Hansens describing the preparation of the compound (melting point reported: 70 - 72°) from pentaerythritol and 66% hydrobromic acid¹⁷.

Treatment of pentaerythrityl monobromide with alcoholic potassium hydroxide¹⁸, followed by separation

3,3 bis-(hydroxymethyl)-oxacyclobutane (I). This product was obtained in 55 - 70% yield.

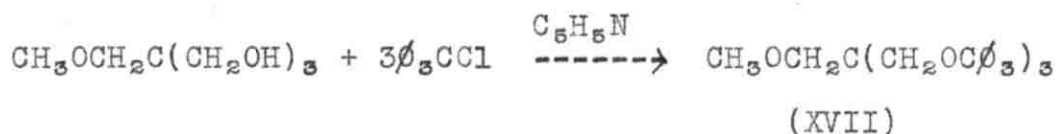
The reaction of (I) with methyl, ethyl- and n-propyl alcohols was carried out at room temperature. The general procedure followed, was to treat the cyclic compound with an excess of the alcohol in the presence of catalytic amounts of sulfuric or p-toluene sulfonic acids, allow the mixture to stand for about two days, then neutralize with sodium bicarbonate and remove the excess alcohol by distillation. The products were isolated directly, or acetylated and then transesterified.

The reaction of 3,3 bis-(hydroxymethyl)-oxacyclobutane (I) with methyl alcohol proceeded smoothly to give the monomethyl ether of pentaerythritol (VII) in very good yield:



The crude product was contaminated by some impurity that caused oil formation during the recrystallization process. This difficulty was eliminated completely by exhaustive extraction of the product in a Soxhlet extractor with dry ether. In this manner, monomethyl pentaerythrityl ether, melting at 67 - 68°, was obtained in 82% yield. Recrystallization from a chloroform-ethyl acetate mixture raised the

m. p. to 71 - 72°. Esterification of the crude product with acetic anhydride in the presence of pyridine¹⁹ gave the triacetate of monomethyl pentaerythrityl ether, boiling at 117 - 120°/1 mm., yield: 71%. This ester gave saponification equivalents of 91 and 91.5 (Calculated for the triacetate of VII: 92). Transesterification with sodium ethoxide in ethanol gave VII. Treatment of the crude ether (VII) with triphenylchloromethane²⁰ in pyridine gave the corresponding trityl ether (XVII) in good yield:



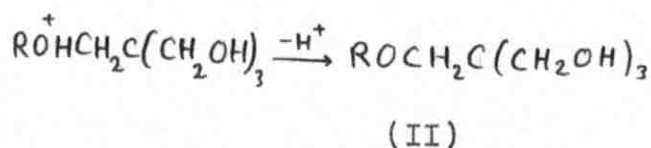
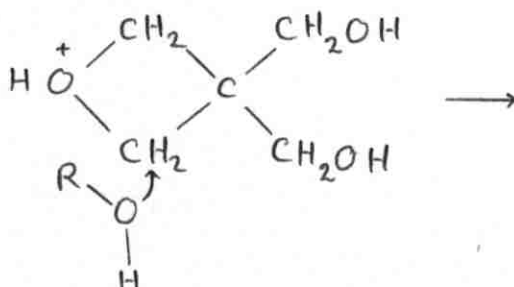
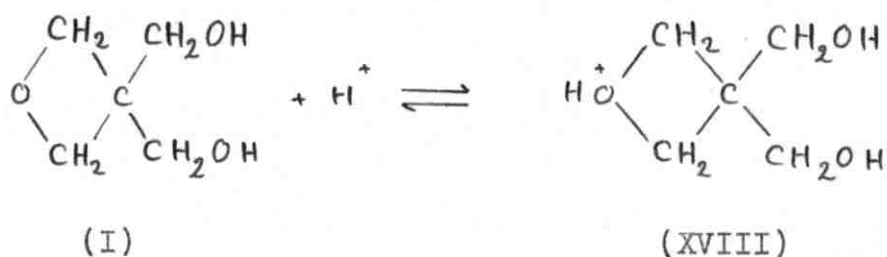
The preparation of pentaerythrityl monoethyl ether was not as clean cut as that of the monomethyl ether. When sulfuric acid was used as a catalyst, the reaction between (I) and ethyl alcohol gave 27 - 33% yield of the expected ether, isolated as the triacetate by fractional distillation. However, an appreciable amount of higher boiling fractions was also obtained. One of these fractions was identified as pentaerythrityl tetraacetate. Another fraction (probably a polymer) partly decomposed during the distillation at 230°/ 1 mm. Substitution of p-toluene sulfonic acid for sulfuric acid gave the same yield of the monoethyl ether together with a high boiling fraction which could not be distilled due to extensive decomposition.

No definite products could be isolated from the

reaction of n-propyl alcohol with 3,3 bis-(hydroxymethyl) oxacyclobutane, under the experimental conditions used in this investigation. The reaction mixture distilled over a wide range, with appreciable quantities of high boiling fractions present.

DISCUSSION

The acid-catalyzed opening of the oxide ring of 3,3 bis-(hydroxymethyl)-oxacyclobutane (I) by alcohols, probably proceeds in a manner similar to the analogous reaction with ethylene oxides¹:



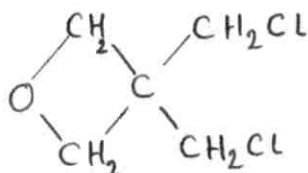
The catalyst functions by coordination with the oxide (I) to give the conjugate acid (XVIII), in which the carbon-oxygen linkage is greatly weakened. The second step of the reaction represents a nucleophilic displacement on carbon, the ring oxygen atom functioning as the displaced group.

The reaction of (I) with methyl alcohol gave monomethyl pentaerythrityl ether (II, R = methyl). This compound could be separated very easily from a small amount of a high melting solid formed as a side-product (probably a polymer), by exhaustive extraction with ether. Recrystallization of the product gave pure monomethyl pentaerythrityl ether, melting at 71 - 72° (73°, for the analytical sample), in very good yield. Previous methods for the preparation of this compound gave unsatisfactory yields,^{11,13} while a recent patent describing its preparation reports a melting point of 60 - 67°¹⁵.

The appreciable drop in the yield of monoethyl pentaerythrityl ether formed from the reaction of (I) with ethyl alcohol, and the failure of n-propyl alcohol to give any well-defined products is unexpected. However, a similar, but less pronounced, decrease in yield is reported in a recent work by Searles and Butler¹⁶ for the reaction between trimethylene oxide and a series of alcohols. The yields of the corresponding 3-hydroxypropyl-alkyl ethers from methyl, ethyl, n-propyl and n-butyl alcohols were reported as 69%, 58.6%, 55.4% and 45% respectively, while the yield with benzyl alcohol was as low as 23.2%.

The formation of polymeric side-products obtained in the course of this investigation has also been observed in the analogous reactions of trimethylene oxides¹⁶ and ethylene oxides¹. A similar type of polymerization has

been reported recetly for the compound 3,3 bis(chloromethyl) oxacyclobutane (XIX)²¹:



(XIX)

It is claimed that polymerization of (XIX) does not take place in a system from which water is rigorously excluded. Thus, a stable solution of XIX and boron trifluoride is obtained in dry methyl chloride, which, however, starts polymerizing immediately when even traces of water are added, to give a polyether of the type $\left(\text{OCH}_2\text{C}(\text{CH}_2\text{Cl})_2\text{CH}_2\right)_n$.

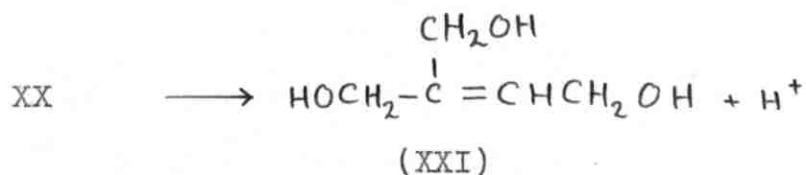
The publication describing the preparation of 3,3 bis-(hydroxymethyl) oxacyclobutane¹⁸ from pentaerythryl monobromide and potassium hydroxide makes mention of a side-product isolated during the final distillation of the reaction mixture but gives no further details. Investigation of this product showed that it was unsaturated, since it gave distinctly positive tests with bromine in carbon tetrachloride and with a solution of potassium permanganate. The formation of an unsaturated compound in the course of this reaction could conceivably have arisen from a solvolytic reaction of the monobromide (XV) followed by a 1,2 shift of a hydroxymethyl group to give the carbonium ion (XX). This

would immediately lose a proton to give (XXI):



(XV)

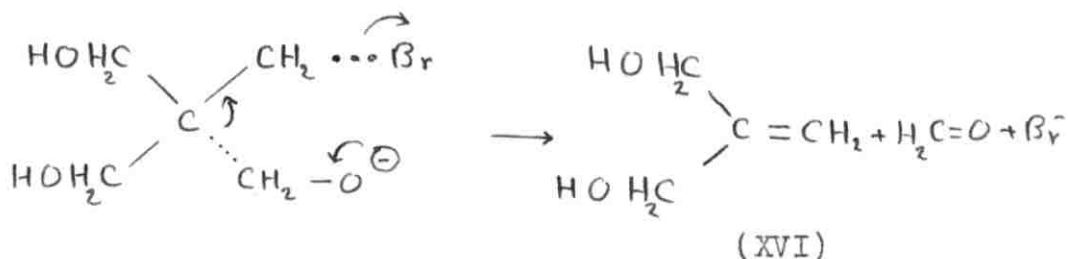
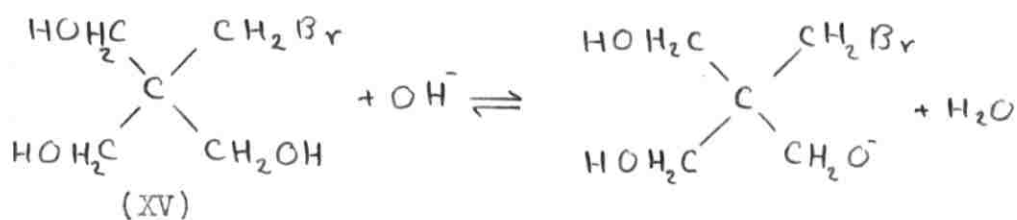
(XX)



This type of mechanism has been shown to be characteristic of the reactions of neopentyl halides, under certain environmental conditions²². However, the possibility of such a reaction was considered unlikely on the basis of the following arguments: 1. The trihydroxy compound (XXI) would be expected to have a boiling point higher than the observed one (93 - 95°/ 1 mm.). 2. Under the experimental conditions of the reaction (alcoholic potassium hydroxide, with only traces of water present in the reaction mixture) the above mechanism is extremely unlikely.

The second possibility was that of an elimination reaction operating along the chain of the 1,3 bromohydrin moiety of (XV), giving 3 hydroxy-2-hydroxymethyl-1-propene

(1,3 propenediol-2-methylene) (XVI):



This reaction is analogous to the usual elimination reaction which invariably accompanies substitution at a saturated carbon atom, but which is prohibited here because of the absence of β -hydrogen atoms²³. A few other examples of this type of elimination reaction have been reported recently in the literature^{24,25,23}.

The physical constants of the unsaturated compound checked with those reported for 3-hydroxy-2-hydroxymethyl-1-propene (1,3 propanediol, 2-methylene)²⁶. Furthermore, the compound was esterified with acetic anhydride to give an ester the saponification equivalent of which was found to be identical with that calculated for the diacetate of (XVI). The identification of the compound was completed by the preparation of its dichloride (XXII), the physical constants of which checked with those reported in the literature

for 3-chloro-2-chloromethyl-1-propene²⁶.

EXPERIMENTAL

Preparation of Pentaerythrityl Monobromide

The procedure adopted for the preparation of this compound was a modification of the method used by Beyaert and Hansens¹⁷.

In a 3 liters two-necked E flask fitted with a dropping funnel and a reflux condenser were placed 200 g (1.47 moles) of pentaerythritol, 1.5 liters of glacial acetic acid and 17 ml of 48% hydrobromic acid. The mixture was refluxed for 1.5 hours. Then, to the boiling solution were added 170 ml of 48% hydrobromic acid and the solution was refluxed for 3 hours. At the end of this time, 96 ml of 48% hydrobromic acid were added and the refluxing was continued for 3 more hours. The solution was heated under reduced pressure to remove as much of the acetic acid and water as possible and was finally heated for 15 minutes at 140 - 150°/ 10 mm. The viscous residue was treated with 750 ml of 98% ethyl alcohol and 50 ml of 48% hydrobromic acid. The flask was provided with a fractionating column and the solution was fractionated slowly until about 500 ml of distillate were collected. Then, a second 750 ml portion of ethyl alcohol was added and the fractionation was continued slowly until 750 ml more distillate were collected. (The boiling point during the collection of the

first 500 ml of distillate remained constant at 71 - 72°, corresponding to the ethanol-ethyl acetate azeotrope; it rose slowly to 78° during the collection of the second portion of the distillate). The flask was fitted with a Claisen head and a condenser set for downward distillation and the remaining alcohol was removed as completely as possible under reduced pressure. Benzene (500 ml) was added to the residue and distilled off at atmospheric pressure, finally heating to 140°/10 mm. The same procedure was repeated with a second 500 ml. portion of benzene, in order to ensure complete removal of water from the residue. The viscous residue was then refluxed for several hours with 500 ml of dry ether with frequent shaking until it became white and granular. After cooling thoroughly, the ether was decanted and the solid washed twice with two 200 ml portions of dry ether. The product was then extracted exhaustively with 600 ml. of dry ether in a Soxhlet extractor. The ether extract was cooled overnight in the refrigerator and the precipitated monobromopentaerythritol was collected by filtration and washed with 200 ml of cold, dry ether. The yield of crude product melting at 70 - 72° was 145 - 160 grams (49 - 54%). One recrystallization from a mixture of 120 ml chloroform and 80 ml ethyl acetate raised the melting point to 75 - 76°.

recovery 85%*.

Preparation of 3,3 bis-(Hydroxymethyl)-Oxacyclobutane

The procedure adopted for the preparation of this compound was a modification of the method of Govaert and Beyaert¹⁸.

In a 500 ml 2-necked round-bottom flask fitted with a mechanical stirrer and a reflux condenser were placed 39.8 g (0.2 moles) of pentaerythrityl monobromide and 160 ml of absolute ethyl alcohol. The mixture was stirred at room temperature until all the monobromide dissolved. To the solution was then added potassium hydroxide (13 g; 0.23 moles) dissolved in absolute ethyl alcohol (190 ml). The solution was stirred for two hours at room temperature and then refluxed on the steam bath for five minutes. The mixture was cooled and the precipitated potassium bromide removed by filtration. The filtrate was neutralized with acetic acid and the alcohol removed under reduced pressure. The residual oil was distilled through a Vigreux column. Two fractions were obtained:

* Dibromopentaerythritol, formed as a side-product, is present in the ether extracts. At the end of the extraction, 30 - 35 g. of unreacted pentaerythritol remained in the extraction thimble.

Fraction I: 3 - 4 g, collected between 85 - 100°/1mm.

Fraction II: 13 - 16.5 g, (55 - 70% of the theoretical) of 3,3 bis-(hydroxymethyl) oxacyclobutane, boiling at 135 - 138°/ 1 mm.

Characterization and Reactions of Fraction I

Physical Constants: Refractionation of this fraction gave a colorless liquid boiling at 93 - 95°/ 1-2 mm.

n_D^{25} 1.4731; d_4^{27} 1.077. (Literature values for 1,3-propanediol, 2 methylene²⁶: b.p. 125 - 126°/ 18 mm., n_D^{20} 1.4758 d_4^{20} 1.0791.)

Qualitative Tests: Tests with bromine in carbon tetrachloride, potassium permanganate and ceric nitrate were all positive.

Esterification of Fraction I: In a 200 ml round-bottomed flask fitted with a reflux condenser protected by a calcium chloride tube, were placed 10 g of Fraction I, 80 g of acetic anhydride and 1 ml of dry pyridine¹⁹. The mixture was heated on the steam bath for 12 hours. The excess acetic anhydride was then distilled off under reduced pressure. The residue was cooled and poured with stirring onto 100 g of ice. The mixture was neutralized with sodium bicarbonate and extracted with five 50 ml portions of ether. The combined ether extracts were washed once with water saturated with sodium chloride and then dried over anhydrous sodium sulfate and filtered. The ether was

removed by distillation and the residual oil distilled under reduced pressure. The yield of ester, boiling at 85 - 87°/1 mm, was 17.5 g (90% of the theoretical). Saponification equivalent calculated for the diacetate of 1,3-propanediol, 2 methylene: 86. Found 86. n_D^{20} 1.4350; d_4^{28} 1.072.

Preparation of 3-Chloro-2-Chloromethyl-1-Propene: In a 100 ml E three-necked flask provided with a condenser (protected by a calcium chloride tube on top), a mercury-sealed stirrer and a dropping funnel, were placed 8.8 g (0.1 moles) of 1,3-propanediol, 2-methylene, 15 ml of dry pyridine and 10 ml of dry chloroform. The flask was cooled in an ice-bath and 29 g of thionyl chloride dissolved in 20 ml of dry chloroform were added through the dropping funnel in the course of two hours, while stirring vigorously. The mixture was refluxed for two hours and then allowed to stand overnight at room temperature; it was then neutralized by pouring onto a mixture of ice and solid sodium bicarbonate and allowed to stand for five hours with occasional stirring. The resulting mixture was extracted with ether and the ether extracts were washed with dilute sulfuric acid dried over sodium sulfate and filtered. Removal of the ether, followed by distillation of the residual oil gave 3.2 grams of a colorless liquid boiling at 137 - 138°/ 756 mm, n_D^{28} 1.4720, d_4^{27} 1.178. (Literature values²⁶ for 3-chloro-2-chloromethyl-1-propene: b.p. 138 - 138.3°,

n_D^{20} 1.4754, d_4^{20} 1.1782.)

Preparation of Pentaerythrityl Monomethyl Ether

A solution of 22 g (0.186 moles) of 3,3 bis-(hydroxymethyl)-oxacyclobutane in 60 ml of methyl alcohol was added by means of a dropping funnel to a 250 ml round-bottomed flask containing 65 ml of methyl alcohol and 0.25 ml of concentrated sulfuric acid. The addition took about five minutes. The solution was kept at room temperature for 45 - 50 hours and then neutralized with 1 g of sodium bicarbonate. The mixture was cooled in an ice-bath and filtered. The filtrate was heated under reduced pressure to remove the methyl alcohol completely. The viscous residue solidified on standing. The solid was refluxed with 25 ml of dry ether. The ether was decanted and the residue dried thoroughly in a vacuum desiccator and then powdered and extracted in a Soxhlet extractor for twelve hours with 100 ml of dry ether. The ether extract was cooled thoroughly and filtered to give 23 g (82% of the theoretical) of monomethyl pentaerythrityl ether, melting at 67 - 68°. One recrystallization from a mixture of 12 ml chloroform and 8 ml ethyl acetate raised the melting point to 71 - 72°, recovery 85 - 94%. The analytical sample melted at 72 - 73°.

Anal. Calcd. for $C_6H_{14}O_4$: C, 47.98; H, 9.40

Found : C, 48.46; H, 9.29

Preparation of Monomethyl Pentaerythrityl Triacetate

Acetylation of the crude monomethyl pentaerythrityl ether (17.6 g ; 0.117 moles) was effected with 110 g. (120ml) of acetic anhydride and 1 ml of dry pyridine by a procedure similar to the one described previously for the esterification of Fraction I. The yield of the ester, boiling at 117 - 119°/ 1 mm, was 23 g. (71% of the theoretical).

n_D^{20} 1.4408; d_4^{28} 1.119.

Saponification equivalent calcd.: 92; Found: 91.5.

Anal. Calcd. for $C_{12}H_{20}O_7$: C, 52.17; H, 7.30

Found : C, 52.32; H, 7.23

Preparation of Monomethyl Pentaerythrityl Tritrityl Ether

Preparation of Triphenyl Chloromethane²⁷: A

mixture of 50 g of triphenyl carbinol and 16 ml of dry benzene was placed in a 250 ml round-bottomed flask provided with a reflux condenser protected by a calcium chloride tube on the top. The mixture was heated on the steam bath. When it was hot, 10 ml of acetyl chloride were added through the top of the condenser. Heating was continued while the mixture was shaken vigorously. In about five minutes all the solid triphenyl carbinol disappeared and a clear solution resulted. In the course of ten minutes an additional 20 ml of acetyl chloride was added in 2 ml portions, and the solution was refluxed for one half hour longer. The solution was then cooled by shaking the flask under running water, and, during this operation,

40 ml of petroleum ether were added through the top of the condenser. The mixture was cooled in an ice bath and the product was filtered and washed with 20 ml of petroleum ether. The colorless solid, after drying in a vacuum desiccator over soda lime and paraffin wax, weighed 42 g and melted at 108 - 110°

Tritylation of Monomethyl Pentaerythryl Ether²⁰: In a 50 ml flask protected by a calcium chloride tube were placed 1.2 g (0.08 moles) of crude monomethyl pentaerythryl ether, 12 ml of dry pyridine and 7.3 g (0.026 moles) of triphenyl chloromethane. The mixture was heated on the steam bath for 1.3 hours and then cooled thoroughly in an ice bath. The crude solid product was removed by filtration and transferred into a mortar where it was triturated with several 10 ml portions of cold water. The solid was powdered thoroughly and washed first with a mixture of water and 95% ethanol and then with water. The product was dried in a vacuum desiccator over phosphorous pentoxide and paraffin wax and then refluxed for five minutes with a mixture of 12 ml of absolute ethyl alcohol and 3 ml of acetone. The solvent was decanted and the solid dried in a vacuum desiccator. One recrystallization from 50 ml of acetone gave 4.2 g (60%) of product melting at 219 - 220°.

Anal. Calcd. for $C_{85}H_{56}O_4$: C, 86.26; H, 6.43

Found : C, 86.03; H, 6.50

Preparation of Monoethyl Pentaerythrityl Ether

A procedure similar to the one used for the preparation of the monomethyl ether was followed. In this case, 26 g (0.22 moles) of 3,3 bis-(hydroxymethyl) oxacyclobutane were treated with 150 ml of commercial absolute ethyl alcohol and 0.25 ml of concentrated sulfuric acid. After removal of the solvent under reduced pressure, the residue was esterified with 220 ml of acetic anhydride and 1 ml of pyridine as described previously. Fractionation of the residual oil gave three fractions.

Fraction I: b.p. 125 - 135°/ 1 mm;

Fraction II: b.p. 145 - 165°/ 1 mm;

Fraction III: b.p. 190 - 230°/ 1 mm.

Fraction I, upon refractionation, gave 17.2 - 21 g of a product (27-33%) boiling at 128-132°/1 mm. Saponification equivalent found: 96, 95.5 (Calculated for monoethyl pentaerythrityl triacetate: 96.6). n_D^{20} 1.4377

Anal. Calcd. for $C_{13}H_{22}O_7$: C, 55.77; H, 7.64

found: C, 54.10; H, 7.65

Transesterification of Fraction I: To a solution of 8.7 g (0.03 moles) of Fraction I in 50 ml of absolute ethyl alcohol was added 0.06 g of sodium dissolved in 100 ml of absolute ethyl alcohol. The solution was refluxed for 1.5 hours and then fractionated slowly through a 40 cm column packed with glass beads. When about 130 ml of distillate were collected

the fractionation was interrupted and the solution was neutralized with dilute hydrochloric acid. After cooling for several hours, the mixture was filtered and the filtrate heated under reduced pressure to remove completely the excess alcohol. The oily residue was then distilled under reduced pressure through a Vigreux column. The yield of monoethyl pentaerythrityl ether, boiling at 142 - 147°/ 1 mm, was 3.1 g (62% of the theoretical).

Fraction II, upon refractionation, gave 5 g of a product, boiling at 145 - 155°/ 1 mm, which solidified on standing. Recrystallization from ethyl alcohol gave 4 g of a solid, melting at 83°. (M.P. reported in the literature for pentaerythrityl tetraacetate: 84 - 86°). Saponification equivalent found: 77. (Calculated for pentaerythrityl tetraacetate: 76).

Fraction III, upon refractionation, gave 6 g of a product boiling at 220 - 230°/1 mm. Some decomposition occurred during the distillation. A non-volatile residue remained in the flask.

Substitution of p-toluene sulfonic acid (1 g) for sulfuric acid as a catalyst for the reaction between 3,3 bis-(hydroxymethyl)-oxacyclobutane and absolute ethyl alcohol did not improve the yield of the monoethyl pentaerythrityl ether. An appreciable quantity of a non-volatile solid was formed, but no pentaerythrityl tetraacetate could be isolated.

Reaction between 3,3 bis-(Hydroxymethyl) Oxacyclobutane
and n-Propyl Alcohol

A procedure similar to the one described previously was followed, using 3,3 bis-(hydroxymethyl)-oxacyclobutane, p-toluene sulfonic acid and excess of n-propyl alcohol. Distillation of the reaction mixture gave a liquid distilling over a wide temperature range (120 - 170°), and a non-volatile residue. No definite product could be isolated from the reaction mixture after esterification.

ACKNOWLEDGMENT

The author wishes to express her thanks to Professor Dr. Georg Maria Schwab and Professor Dr. Hans Geyer, of the University of Munich, for the microanalysis.

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