PENTAERYTHRITOL DERIVATIVES

STUDIES

ON

3-HALOMETHYL-3-HYDROXYMETHYL OXETANES

BY

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ABSTRACT

3-bromomethyl-3-hydroxymethyl oxacyclobutane was prepared in 71% yield by the action of sodium ethoxide on pentaerythrityl dibromide in absolute ethyl alcohol. The structure of this compound was proved by its conversion to pentaerythrityl dibromide by the action of 48% hydrobromic acid, and to 2,6 dioxaspiro (3,3) heptane by the action of potassium hydroxide.

The spirocyclic compound was also prepared in 16% yield by the action of potassium hydroxide on pentaerythrityl dibromide. The compound was found to be sensitive to halogen acids. Thus treatment with 48% hydrobromic acid gave 69% yield of pentaerythrityl dibromide[2]. Similarly, treatment of the spirocyclic compound with lithium aluminum hydride gave neopentyl glycol in 60% yield. This is the first example reported in the literature for the reduction of a trimethylene oxide type of compound by lithium aluminum hydride.

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INTRODUCTION

Previous attempts to prepare 3-halomethyl-3-hydroxymethyl oxacyclobutane (II) by the action of sodium ethoxide on pentaerythrityl dihalide (I) gave 39-43% yield of an impure product[1].

The purpose of the present work was to prepare the 3-chloromethyl-3-hydroxymethyl oxacyclobutane (II, X = Cl) pure, and in better yields, and to investigate further the reaction between pentaerythrityl dibromide (I, X = Br) and sodium ethoxide in absolute ethyl alcohol.

(I) (II)

HISTORICAL

Studies on preferential one sided dehydro halogenation of pentaerythrityl dihalide (I) with sodium ethoxide in ethyl alcohol have been carried out by some investigators[1,2].

Recently it has been reported that the action of sodium ethoxide on pentaerythrityl dichloride[1] (I, X=Cl) gives the corresponding 3-chloromethyl-3-hydroxymethyl oxacyclobutane (II, X=Cl) in 39-43% yield.

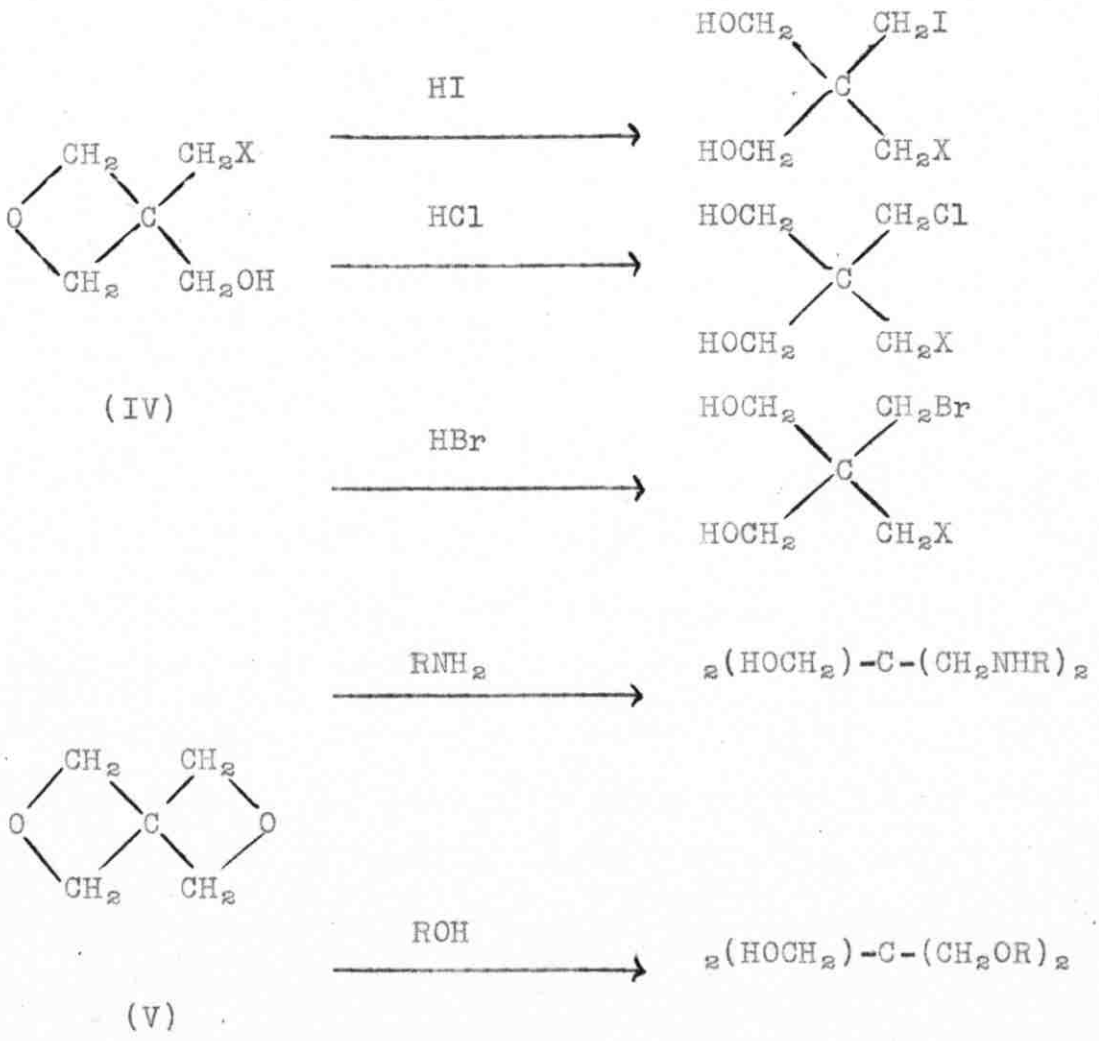
Similarly, dehydrohalogenation of pentaerythrityl monohalide (III) by alcoholic potassium hydroxide[2,3,4,5] has been carried out recently.

(III) (IV)

The possibility of two sided dehydrohalogenation of pentaerythrityl dihalide (I) to the corresponding 2,6-dioxaspiro (3,3) heptane (V) have been recently studied too. Thus the action of potassium hydroxide on pentaerythrityl dichloride[1] (I, X=Cl), or pentaerythrityl dibromide diacetate[4], sulfuric acid on pentaerythritol[4] have been proved to be of no use. The spirocyclic compound (V) was finally obtained in 20-25% yield by the

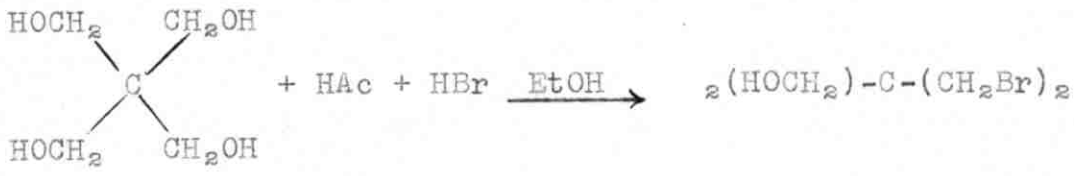
action of potassium hydroxide on pentaerythrityl dibromide[4,5,6] (I, X = Br).

Recent interest in these compounds stems from the fact that the trimethylene oxide ring is sensitive to attack by amines[7], alcohols[8], and halogen acids[1,2,4] thus providing a possible route for the synthesis of amino, ether, and mixed halide derivatives of pentaerythritol not easily available by more direct methods.



RESULTS

The starting material pentaerythrityl dibromide (VII) was prepared from pentaerythritol (VI) and 48% hydrobromic acid by the following reaction which is essentially a modification of the procedure of Beyaert and Hausens[9].



(VI) (VII)

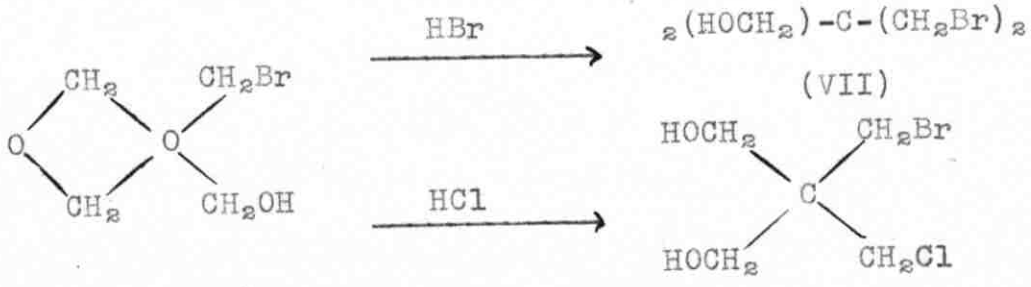
The action of 48% hydrobromic acid on pentaerythritol in glacial acetic acid followed by transesterification of the bromoacetate, and recrystalization of the crude product, gives 63% yield of pentaerythrityl dibromide (VII) melting at 110-111°. This reaction is always accompanied by a sequence of side reactions producing small amounts of pentaerythrityl tribromide and pentaerythrityl monobromide, which can be removed from the main product by recrystalization from benzene and from water respectively.

Treatment of compound (VII) with equivalent amounts of sodium ethoxide in absolute ethyl alcohol followed by filtration and concentration in vacuo gave a viscous oil containing bromine which was later on identified as 3-bromomethyl-3-hydroxymethyl oxacyclobutane (VIII) presumably

a new compound. The product was isolated in a pure state in 71% yield boiling at 141-143/3 mm.

By a similar method 3-chloromethyl-3-hydroxymethyl oxacyclobutane (II, X=Cl) was prepared in 70% yield by the action of sodium ethoxide on pentaerythrityl dichloride (I, X=Cl). The same compound had been previously prepared in 39% yield by the action of excess sodium ethoxide on pentaerythrityl dichloride[1] (I, X=Cl). Substitution of methyl alcohol for ethyl alcohol yielded the same product in 43% yield[1].

Compound (VIII) was found to be extremely sensitive to attack by halogen acids. Thus treatment of 3-bromomethyl-3-hydroxymethyl oxacyclobutane (VIII) with 48% hydrobromic acid or concentrated hydrochloric acid gave pentaerythrityl dibromide (VII) and 2-chloromethyl-2-bromomethyl 1,3 propane diol (pentaerythrityl monochloride monobromide) (IX) respectively in good yields.

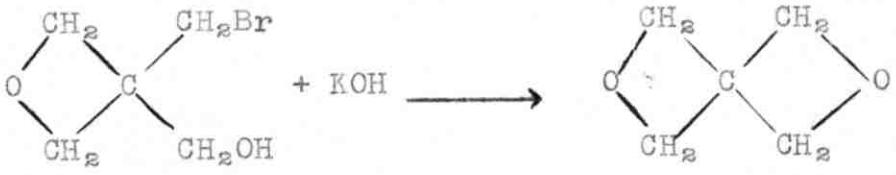


(VIII)

(IX)

The above reactions furnished a partial proof for the structure assigned to compound (VIII). Further evidence for this structure is furnished by the fact that upon treat-

ment of 3-bromomethyl-3-hydroxymethyl oxacyclobutane (VIII) with fused potassium hydroxide followed by distillation in vacuum, 2,6-dioxaspiro (3,3) heptane is formed in 32-35% yield.



(VIII) (V)

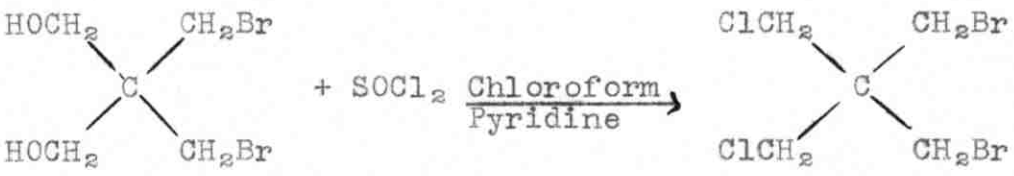
The same compound (V) was prepared independently in 16% yield by the action of fused potassium hydroxide on pentaerythrityl dibromide (VII).

The spirocyclic compound (V) was found to be sensitive to attack by halogen acids[2,4]. Thus treatment with 48% hydrobromic acid or concentrated hydrochloric acid gave dibromo pentaerythritol (VII) and dichloro pentaerythritol (I, X=Cl) respectively in good yields.

Since it was known that 1,2 epoxides reacted with lithium aluminum hydride to give the corresponding alcohol[10], a similar reaction was attempted on 2,6 dioxaspiro (3,3) heptane (V) in an effort to confirm its structure. This reaction proceeded smoothly, as expected, to give 60% yield of neopentyl glycol (X).

(V) (X)

The reaction between dibromo pentaerythritol (VII) and thionyl chloride in the presence of chloroform and small amounts of pyridine[11] gave 2,2 bis(bromomethyl)1,3-dichloro propane (XI) in good yields, presumably a new compound.



(VII) (XI)

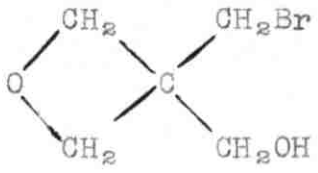
DISCUSSION

In a previous paper[1] it has been reported that the reaction between pentaerythrityl dichloride (I, X= Cl) and sodium ethoxide in ethyl alcohol gives a compound containing chlorine and hydroxyl groups to which the structure of 3-chloromethyl-3-hydroxymethyl oxacyclobutane (II, X = Cl) was assigned. Furthermore, it was stated that the yields of this compound never exceeded 43% of the theoretical, and it was often contaminated with small amounts of 2,6-dioxaspiro (3,3)-heptane (V).

During this investigation it was found that the yields of compound (II, X = Cl) can be improved remarkably (71% of the theoretical) by using equivalent amounts of sodium ethoxide and pentaerythrityl dichloride (I, X = Cl) in absolute ethyl alcohol with continuous stirring at reflux temperatures. No formation of the spirocyclic compound (V) was noticed during this reaction.

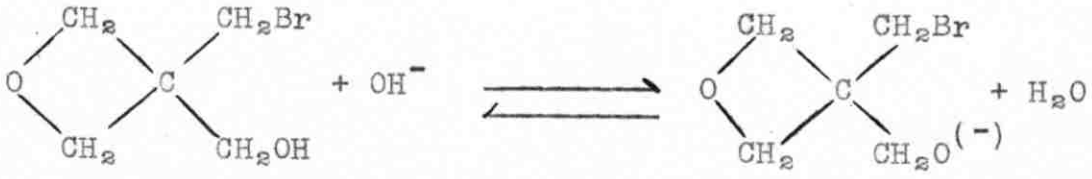
Similarly the reaction between pentaerythrityl dibromide (VII) and sodium ethoxide in absolute ethyl alcohol gave a viscous oil containing bromine and hydroxyl groups, which upon treatment with 48% hydrobromic acid or concentrated hydrochloric acid gave dibromopentaerythritol (VII) and pentaerythrityl monobromide monochloride[1] (IX) respectively in good yields. In view of these facts the structure, 3-bromomethyl-3-hydroxymethyl oxacyclobutane (VIII) was

assigned to the compound.



(VIII)

Further evidence confirming the structure assigned above was found in the fact that treatment of compound (VIII) with fused potassium hydroxide in the presence of small amounts of water gave 2,6 dioxaspiro (3,3) heptane (V) in 32-35% yield. During this reaction a small amount of a light liquid with a sharp odour was isolated. Investigation showed that it was unsaturated since it gave distinctly positive tests with bromine in carbon tetrachloride and with a solution of potassium permanganate. Further tests showed that the compound contains no halogen or hydroxyl groups. The formation of an unsaturated compound in the course of this reaction is probably the result of an elimination reaction[8] giving perhaps 2-methylene 1,3 oxacyclobutane (XII).



(VIII)

(XII)

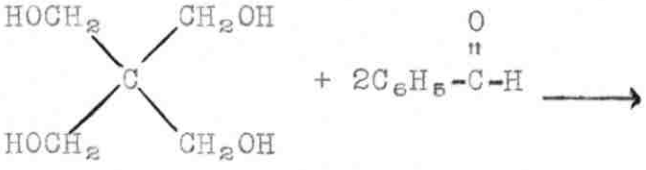
Several examples of this type of elimination reaction have been reported recently in the literature[8,12,13,14].

It has been reported that the reaction between lithium aluminum hydride reagent and organic compounds such as epoxides[10], alkyl halides[10], and toluene sulfonic esters[15] involve essentially the displacement of a strongly electronegative element on carbon by hydrogen. Thus hydrogen is transferred as a hydride trough a bimolecular neucleophilic displacement mechanism[10] and, as a consequence, the neutral aluminum hydride probably coordinates with the alkoxide ion through a sequence of bimolecular reactions thus forming $AL(OR)_4^-$.

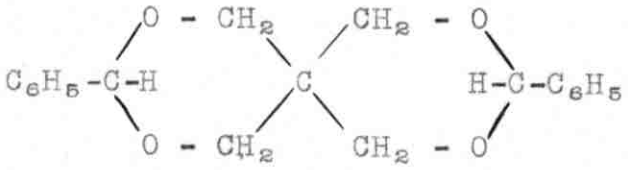
Evidence supporting this mechanism has been demonstrated by Trevoy and Brown[10]. Hence the mode of ring opening of unsymetrical epoxides or sodium ethyl malonate[16,17] proceeds through neucleophilic displacement mechanism followed by inversion of configuration.

A similar mechanism may hold for the reduction of the spirocyclic compound (V) via lithium aluminum hydride reagent. The product of the reduction was identified as 2,2 dimethyl 1,3 propane diol (neopentyl glycol) (X).

At this point it was of interest to see whether a similar reduction could be carried out on acetals. Dibenzal pentaerythritol (XIII) which could be prepared from benzaldehyde and pentaerythritol in the presence of catalytic amounts of hydrochloric acid, was used as starting material.



(VI)



(XIII)

However, when lithium aluminum hydride in tetrahydro furan solution was added to dibenzal pentaerythritol at reflux temperatures, the starting material (XIII) was recovered quantitatively, proving that reduction does not take place.

EXPERIMENTAL

Preparation of Pentaerythrityl Dibromide (VII): The procedure described below is a modification of a method described by Bayaert and Hansens[9].

In a 5 liter two necked round bottom flask equipped with a dropping funnel and a reflux condenser were placed 360 g (2.64 moles) of pentaerythritol, 2160 ml of glacial acetic acid and 28.8 ml of 48% hydrobromic acid. The mixture was refluxed for 1 hour. Through the dropping funnel 1225 ml of 48% hydrobromic acid was introduced dropwise, and the mixture was refluxed for 20 hours. The solution was next heated under reduced pressure to remove as much of the acetic acid and water as possible, and finally it was heated for 1.5 hours at 100-110°/1 mm.

The residue was next treated with 900 ml of absolute ethyl alcohol and 90 ml of 48% hydrobromic acid in a flask provided with a fractionating column. The solution was fractionated slowly until 840 ml of the distillate was collected. The boiling point during this distillation remained constant at 71°, corresponding to the ethanol-ethyl acetate azeotrope. At the end it rose slowly to 78°. A second 900 ml portion of ethanol was introduced to the flask, and in a similar fashion 900 ml of the distillate were collected. During this procedure the distilling temperature remained almost constant at 78°.

The flask was fitted with a condenser set downward for distillation and the alcohol was removed at reduced pressures (100-110°/3 mm). The residue, upon cooling, solidified into yellow crystals which upon refluxing with 1050 ml of benzene went into solution, except small amounts of monobromohydrin which remained a separate layer from the benzene. The solution was cooled in the refrigerator for 2 hours and the precipitated dibromo pentaerythritol was collected by filtration. The product was dried in vacuum desiccator over paraffin wax for one day, and then refluxed with 750 ml of water and 3 grams of charcoal. The solution was filtered while hot and cooled in an ice box for several hours. The precipitate white crystals of dibromo pentaerythritol were collected by filtration and dried. The yield of pentaerythrityl dibromide, melting at 110-111°, was 440 g (63.5% of the theoretical).

Preparation of 3-Bromomethyl-3-Hydroxymethyl Oxacyclo Butane (VIII): In a 1 liter three necked ℬ flask equipped with a mechanical stirrer, condenser, and a dropping funnel, were placed 80 g (0.305 moles) of pentaerythrityl dibromide and 150 ml of absolute ethyl alcohol. The mixture was stirred at room temperature until a clear solution resulted. Through the dropping funnel, a solution of sodium ethoxide (prepared from 7.2 g (0.31) moles) of metallic sodium and 350 ml of absolute ethyl alcohol) was introduced slowly. The mixture was stirred at reflux temperatures for 2.5 hours,

cooled in an ice bath, filtered from the precipitated sodium bromide and concentrated in vacuo to a viscous oil. Fractionation through a Vigreux column at reduced pressure gave 39 g (71% of the theoretical) of 3-bromomethyl-3-hydroxymethyl oxacyclo butane boiling at 141-143°/1-2 mm. n_D^{20} 1.5101.

Microanalysis of Bromine in 3-Bromomethyl-3-Hydroxymethyl Oxacyclobutane: The procedure described below is essentially that of Stepanow, as modified by Ruscher[18], based on decomposition of the sample with metallic sodium and monoethanolamine in the presence of dioxane which is used as a moderator.

In a 50 ml ground glass Erlenmeyer flask fitted with an efficient reflux condenser were placed (0.0240 g) of 3-bromomethyl-3-hydroxymethyl oxacyclobutane, 5 ml each of monoethanolamine and dioxane and (0.4 g) of metallic sodium. The mixture was refluxed for half an hour, cooled, and the condenser was washed with distilled water to destroy the excess of sodium. The solution was next titrated with 8N nitric acid using bromophenol blue as an indicator (i.e. to the yellow colour) and 0.5 ml of nitric acid was added in excess.

The solution was transferred to a 200 ml beaker and the bromide was precipitated in the dark by 5% silver nitrate solution. Filtration of the precipitated silver bromide in a gooch crucible, followed by drying for several hours in

the oven gave 0.251 g of silver bromide.

Anal. calcd. for $C_5H_9O_2Br$: Br. 44.14

Found " " " 44.50

Reaction of 3-Bromomethyl-3-Hydroxymethyl Oxacyclo-Butane with Halogen Acids:

Reaction with Hydrobromic Acid. Preparation of 2,2 Bis (Bromomethyl) 1,3,-Propanediol (Pentaerythrityl Dibromide) (VII): A solution of 5 g (0.027 moles) of 3-bromomethyl-3-hydroxymethyl oxacyclobutane is 50 ml of 48% hydrobromic acid was refluxed for half an hour, cooled and diluted to 100 ml. The mixture was then neutralized with sodium carbonate and cooled in an ice bath. Extraction of the mixture with six 30 ml portions of ether followed by drying the combined ether extracts over sodium sulfate and evaporating the ether, gave a white residue which upon recrystalization from water gave 5.7 g (79%) of pentaerythrityl dibromide melting at 110-111°,

A mixture with an authentic sample showed no depression in the melting point.

A similar procedure using 48% of hydrobromic acid and 5 g of 3-bromomethyl-3-hydroxymethyl oxacyclobutane, at room temperature for two days, gave (70%) yield of pentaerythrityl dibromide.

2-Bromomethyl-2-Chloromethyl 1,3 Propane Diol (IX): This compound was prepared from 5 g (0.027 moles) of 3-bromomethyl-3-hydroxymethyl oxacyclobutane (VIII) and 50 ml of

concentrated hydrochloric acid by a method similar to the one described above. The crude product was recrystalized from a mixture of carbon tetrachloride (4 parts) and toluene (1 part) to give 4.24 g (71% of the theoretical) of 2-bromomethyl-2-chloromethyl 1,3 propane diol (IX) melting at 95.5-96°.

A mixture with an authentic sample melted at the same temperature.

2,2 Bis Chloromethyl 1,3 Dibromo Propane (XI): In a 1 liter three necked flask with ground glass fittings equipped with a mechanical stirrer, dropping funnel, and a reflux condenser connected through calcium chloride tube to a gas absorption trap, were placed 80 g (0.305 moles) of pentaerythrityl dibromide, 125 ml of chloroform and 46 ml (0.67 moles) of pyridine. The flask was placed in an ice bath and the mixture was stirred until a clear solution resulted. Through the dropping funnel 129 g (80 ml 0.8 mole) of thionyl chloride dissolved in 80 ml of chloroform were added very slowly. The addition took about 4 hours. Stirring was continued over night and then the mixture was refluxed at 70° for two more hours.

Removal of chloroform and excess of thionyl chloride under reduced pressure gave a yellow residue which was washed several times with hot water to remove unreacted pentaerythrityl dibromide. The crystals were dried and recrystalized from 80-100° petroleum ether. The product was dried over paraffin wax in a vacuum desiccator to give 68.5 g (69.2% of

the theoretical) of 2,2 bis chloromethyl 1,3 dibromo propane melting at 114-118°. The compound was further purified by sublimation in vacuo, melting point 116.5 - 118°.

The product was analyzed for chlorine and bromine as described previously by a method similar to that of Rascher[18] using 0.0368 g of the sample.

Anal. Calcd. for $C_5H_8Cl_2Br_2$: Cl-Br 77.21

Found " " " " 77.10

Preparation of 2,6 Dioxaspiro (3,3) Heptane (V).

Pentaerythrityl Dibromide in Potassium Hydroxide Method: A mixture of 40 g (0.154 moles) of pentaerythrityl dibromide, 150 g (2.63 moles) of potassium hydroxide and 20 ml of water were placed in a 500 ml two necked round bottom ℬ flask equipped with a stirrer and Claisen head attached to a condenser set for downward distillation. The flask was heated in an oil bath at 100° with continuous stirring. After a small forerun of an unsaturated liquid the spirocyclic compound distilled over at 85°/ 15 mm. The compound was then recrystalized from petroleum ether 80-100°, giving 2.5 g (15.6% yield based on pentaerythrityl dibromide) of 2,6 dioxaspiro (3,3) heptane melting at 90 - 91°.

3-Bromomethyl-3-Hydroxymethyl Oxacyclobutane in Potassium Hydroxide Method: In a 500 ml three necked round bottom flask with ground glass fittings, equipped with a stirrer, dropping funnel and a Claisen heat attached to a

condenser set downwards and connected to a vacuum pump were placed 150 g (2.63 moles) of potassium hydroxide and 20 ml of water. The temperature of the bath was raised to 140°, while stirring, and the pressure was maintained at 15 mm. Through the dropping funnel 40 g (0.221 moles) of 3-bromomethyl-3-hydroxymethyl oxacyclobutane were introduced to the reaction flask dropwise. A small amount of an unsaturated liquid distilled over followed by the spirocyclic compound which eventually solidified in the condenser. After the addition was completed the temperature of the bath was raised to 150°/3 mm for half an hour.

The solid was collected and recrystalized from petroleum ether 80-100°, giving 7.8 g (35% yield) of 2,6-dioxaspiro (3,3) heptane melting at 90-91°.

Reaction of 2,6-Dioxaspiro (3,3) Heptane With Halogen Acids.

Reaction with Hydrobromic Acid. Preparation of 2,2-Bis (Bromomethyl) 1,3-Propanediol (Pentaerythrityl Dibromide) (VII): A mixture of 2 g (0.02 moles) of 2,6-dioxaspiro (3,3) heptane, and 50 ml of 48% hydrobromic acid was refluxed for 1 hour. The mixture was then cooled and neutralized with sodium carbonate, and extracted with five 40 ml portions of ether. The combined ether extracts were dried over anhydrous sodium sulfate and filtered. Evaporation of the ether gave a white solid which upon recrystalization from 30 ml of water gave 3.5 g (69% of the theoretical based

on 2,6-dioxaspiro (3,3) heptane) of pentaerythrityl dibromide melting at 110-111°.

A mixture with an authentic sample showed no depression in the melting point.

Similarly the reaction between the spirocyclic compound and 48% hydrobromic acid at room temperatures gave 60% yield of dibromo pentaerythritol melting at the same temperature as above.

Reaction With Hydrochloric Acid. Preparation of 2,2 Bis (Chloromethyl) 1,3,-Propane Diol (Pentaerythrityl Dichloride) (I, X = Cl): As above, a similar procedure was employed using 2 g (0.02 moles) of 2,6 dioxaspiro (3,3) heptane and 50 ml of concentrated hydrochloric acid. Extraction of the solution with ether. Followed by recrystalization of the crude product from a mixture of chloroform, carbon tetrachloride and toluene gave 2.07 g (60% of the theoretical) of 2,2 bis (chloromethyl) 1,3-propane diol melting at 80-81°.

Preparation of 3-Chloromethyl-3-Hydroxymethyl-Oxacyclo Butane (II, X = Cl).

Preparation of Pentaerythrityl Dichloride. (I, X = Cl): The procedure outlined below is a duplication of that described by Gulen[1] in a previous paper.

Monobenzal pentaerythritol was prepared in 74% yield by a modification of Bograchovs[19] procedure. The monobenzal pentaerythritol was converted to monobenzal pentaerythrityl

dichloride by the action of thionyl chloride in the presence of pyridine[11]. Hydrolysis of the product followed by extraction with ether and recrystalization of the crude product from a mixture of chloroform, carbon tetrachloride and toluene gave 71% yield of pentaerythrityl dichloride melting at 80-81°.

Reaction of Pentaerythrityl Dichloride with Sodium Ethoxide in Ethyl Alcohol: A similar procedure for the preparation of 3-bromomethyl-3-hydroxymethyl oxacyclo butane was employed using a solution of 40 g (0.23 moles) of pentaerythrityl dichloride in 150 ml of ethyl alcohol and 5.3 g (0.23 moles) of metallic sodium dissolved in 350 ml of ethyl alcohol.

Stirring of the solution for 2 hours at reflux temperatures followed by cooling, filtering of the precipitated sodium chloride followed by concentration in vacuo, gave a viscous oil. Fractionation through a vigreux column at reduced pressure gave 22.5 g (69% yield) of 3-chloromethyl-3-hydroxymethyl oxacyclobutane boiling at 142-145°/4-5 mm. n_D^{21} 1.4822.

The compound was analyzed for chlorine as described previously by Rascher[18].

Anal. Calcd. for $C_5H_9O_2Cl$: Cl 25.96

Found " " " 26.05

Conversion of 3-chloromethyl-3-hydroxymethyl oxacyclo butane to pentaerythrityl dichloride was accomplished

by refluxing 2.5 g (0.018 moles) of the compound with 25 ml of concentrated hydrochloric acid followed by diluting and extracting the solution with ether. Evaporation of the ether extracts gave a white solid which upon recrystalization from a mixture of chloroform, carbon tetrachloride and toluene gave 70% yield of pentaerythrityl dichloride melting at 80-81°.

A mixture with an authentic sample melted at the same temperature.

Reaction of 2,6-Dioxaspiro (3,3) Heptane with Lithium Aluminum Hydride: In a 500 ml three necked round bottom flask fitted with a mechanical stirrer, dropping funnel and a reflux condenser terminating with a calcium chloride tube were placed 3 g (0.08 moles) of pulverized lithium aluminum hydride reagent and 40 ml of dry tetrahydro furan* [20].

The mixture was stirred under reflux temperatures until most of the solid went into solution. The flask was then cooled to room temperature and a solution of 3.2 g (0.04 moles) of 2,6 dioxaspiro (3,3) heptane in 40 ml of dry tetrahydro furan was added slowly at such a rate that the solution refluxed gently without application of heat. Addition took one hour and the mixture was then stirred at

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*Tetrahydro furan was dried by sodium and then by lithium aluminum hydride added in small portions with continuous stirring until no further reaction ensues. After the mixture was stirred most of the tetrahydro furan was distilled and collected in a receiver protected from moisture by a calcium chloride tube.

reflux temperatures for 8 more hours.

The condenser was set downward for distillation and 50 ml of the tetrahydro furan was removed carefully so as to avoid explosion[21]. The condenser was then set at reflux position and 20 ml of dry ether were added slowly from the dropping funnel followed by 5 ml of ethyl acetate, and finally 40 ml of 6 N hydrochloric acid were added very slowly.

The condenser was again set downward and the dropping funnel was replaced by a tube reaching nearly the bottom of the flask and steam was passed in. Steam distillation was continued until the temperature of the distillate rose to 100°. During this process all the tetrahydro furan, ether, and ethyl acetate was removed and the solution in the flask became clear.

The flask was cooled to room temperature and the solution was extracted with 10 portions of ether of 25 ml each. The combined ether extracts were dried over anhydrous sodium sulfate, filtered and evaporated.

The crude product upon recrystalization from toluene gave 2 g (60% yield) of 2,2-dimethyl (1,3) propane diol (neopentyl glycol) (X) melting at 128-130°.

Mixed melting point with anauthentic sample showed no depression.

Preparation of Dibenzal Pentaerythritol (XIII):

In a 1 liter two necked flask equipped with a mechanical

stirrer and a reflux condenser, were placed 60 g (0.45 moles) of pentaerythritol and 450 ml of water. The mixture was heated while stirred until all the solid went into solution. The flask was allowed to cool to room temperature and 4.4 ml of concentrated hydrochloric acid were introduced to the reaction mixture followed by 120 ml of benzaldehyde. The mixture was stirred for 20 hours at room temperature.

The precipitate formed in the course of this reaction was filtered, washed with sodium carbonate solution, and then refluxed with 500 ml of water made slightly alkali by sodium carbonate and then filtered while hot. The small amount of monobenzal pentaeruthritol formed furing this reaction went into the water whereas the dibenzal pentaerythritol remained as a precipitate which was eventually dried and then recrystalized from 600 ml of n-butyl alcohol, The yield of dibenzal pentaerythritol melting at 159° was 120 g (86% of the theoretical).

Reaction of Dibenzal Pentaerythritol with Lithium Aluminum Hydride: A suspension of 3.7 g (0.095 moles) of lithium aluminum hydride reagent in 50 ml of dry tetrahydro furan was placed in a 500 ml three necked round bottom flask fitted with a stirrer, dropping funnel, and an efficient reflux condenser terminating with a calcium chloride tube.

The mixture was stirred at reflux temperatures for half hour and then allowed to cool to room temperature.

While stirring, a solution of 15.6 g (0.005 moles) of dibenzal pentaerythritol in 100 ml of dry tetrahydro furan was introduced dropwise, and then the mixture was stirred at reflux temperature for 36 more hours.

The condenser was set downward for distillation and about 70 ml of the tetrahydro furan were removed. The condenser was again set at reflux position and 30 ml of ethyl acetate were introduced dropwise followed by 50 ml of 6 N sulfuric acid.

The condenser was again set downward and the mixture was steam distilled until the temperature of the distillate rose to 100°. The flask was cooled and the solution was extracted with 10 portions of ether of 50 ml each. The combined ether extracts were dried over anhydrous sodium sulfate, filtered and evaporated. The crude product upon recrystalization from normal butyl alcohol gave the same starting material almost quantitatively melting at 159°.

A mixture with an authentic sample melted at the same temperature.

SUMMARY

1.- Pentaerythrityl dibromide has been prepared from pentaerythritol and 48% hydrobromic acid in the presence of glacial acetic acid.

2.- The reaction between pentaerythrityl dibromide and sodium ethoxide in ethyl alcohol gives 3-bromomethyl-3-hydroxymethyl oxacyclobutane.

3.- Pentaerythrityl dibromide reacts with thionyl chloride in the presence of pyridine to give 2,2 bis(chloromethyl)-1,3-dichloropropane.

4.- Reaction between 3-bromomethyl-3-hydroxymethyl oxacyclobutane and potassium hydroxide gives 2,6 dioxaspiro (3,3) heptane.

5.- 2,6 dioxaspiro (3,3) heptane can be reduced by lithium aluminum hydride to neopentyl glycol.

6.- Acetals, such as dibenzal pentaerythritol are not reducable by lithium aluminum hydride reagent.

BIBLIOGRAPHY

1.- Gulen, R., M.S. Thesis, American University of Beirut, (1955).

2.- Govaert, F., and Beyaert, M., Proc. Acad. Sci., Amsterdam, 42, 790 (1939). Chem. Abstracts, 34, 5414 (1940).

3.- Matar, A., M.S. Thesis, American University of Beirut, (1955).

4.- Backer, H.J., and Kenning, K.J., Rev. Trav. Chim., 53, 812 (1934). Chem. Abstracts, 28, 5407 (1934).

5.- Furukawa, K., Wada, Y., and Oda, R., Bull. Inst. Chem. Research, Kyoto University, 31, 222 (1953). Chem. Abstracts, 48, 7596 (1954).

6.- Govaert, F., Beyaert, M., Proc. Acad. Sci., Amsterdam, 7, 790 (1939). Chem. Abstracts, 34, 5415 (1940).

7.- Govaert and Cazier, Bull. Soc. Chim. Belge, 54, 43 (1945).

8.- Issidorides and Matar, J. Am. Chem. Soc., 77, 6382 (1955).

9.- Beyaert and Hansens, Natuurw. Tijdschr. (Belg), 22, 249 (1940). Chem. Abstracts, 37, 5373 (1943).

10.- Trevoy and Brown, J. Am. Chem. Soc., 71, 1675 (1949).

11.- Wawzonek, S., and Issidorides, C.H., J. Am. Chem. Soc., 75, 2373 (1953).

12.- Searles, S., and Gotratowski, M.J., J. Am. Chem. Soc.,

75, 3030 (1953).

13.- Snyder, H.R., and Brewster, J.H., J. Am. Chem. Soc., 71, 1061 (1949).

14.- Brewster, H., and Hess, H., Monatsh., 81, 945 (1950).

15.- Kenner and Murray, J. Chem. Soc., 1950, 406.

16.- Grigsby, Hind. Chenley and Westeimer, J. Am. Chem. Soc., 64, 2606 (1942).

17.- Russel and Vanderwerf, J. Am. Chem. Soc., 69, 11 (1947).

18.- Belcher and Godbert, Semi-Micro Quantitative Organic Analysis, Longmans, Green and Co., Ltd. (1954) p. 135.

19.- Bograchov, E., J. Am. Chem. Soc., 72, 2268 (1950).

20.- Organic Synthesis, Vol. 33, 34 (1953).

21.- Barbaras, Barbaras, Finholt and Schlesinges, J. Am. Chem. Soc., 70, 877 (1948).