NEW REACTIONS OF PENTAERYTHRITOL

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By

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INTRODUCTION

Pentaerythritol has been manufactured in large quantities during war-time for conversion to its explosive tetranitrate. It has also a considerable market as a component in resinous compositions for the paint and varnish industry, and is becoming important for manufacturing surface-active agents.

Owing to the polyhydroxylic nature of pentaerythritol the preparation of most of its derivatives described in the literature involves more steps than would be required for an ordinary alcohol. It has been the purpose of this work to enrich the chemistry of pentaerythritol and to investigate especially whether its esterification, etherification, and conversion to amines could be accomplished in a simpler and thus cheaper way.

HISTORICAL

Acetal formation.

In general the method of preparing a diacetal of pentaerythritol involves only mixing an aldehyde, pentaerythritol, and a mineral acid, such as sulfuric or hydrochloric acid, which were used by Tollens (1), Read (2) and Radulescu (3). Mkhitaryan (4) and Backer and Schurink (5) have recommended p-toluenesulfonic acid and zinc chloride respectively as condensing agents.

To restrict aldehydes to monoacetal formation, equimolar amounts of pentaerythritol and the aldehyde have been used, but even then yields are poor, because the formation of the corresponding diacetal cannot be prevented. Skrabal and Kalpasanov (6) separated the so obtained monoacetals from the corresponding diacetal by their different solubilities in hot benzene. A separation by fractional distillation has never been tried.

Esterification with methyl acrylate.

The most important use of the tetraesters of pentaerythritol is in the paint and varnish industry, where they may serve either as synthetic drying oils or resins for making varnishes and enamels. The pentaerythritol tetraacrylate has not been reported in the literature, although it would probably find use as a monomer for making special cross-linked plastics.

In view of the ready availability of methyl acrylate and the difficulties of using the free acid, alcohol exchange was chosen as a route to this tetra-ester. Rehburg (7) has prepared n-butyl acrylate by alcoholysis of methyl acrylate with n-butyl alcohol. This author used hydroquinone as inhibitor and *p*-toluesnesulfonic acid as catalyst. The methanol formed during the reaction was removed by distilling out the methanol-methyl acrylate azeotrope. Berlin and Bogdanov (8) used concentrated sulfuric acid as catalyst for the alcoholysis of methyl methacrylate with ethylene glycol and studied the polymers derived from the glycol dimethacrylate. Blagonravova and Antipova (9) reported that calcium and lead oxides are the most effective catalysts for esterification of vegetable oils with glycerol or pentaerythritol, whereas oxides of iron, cobalt and zinc are ineffective. The same authors claim that caustic alkali, in the form of an alkoxide derived from the alcohol used, is even more effective than calcium or lead oxide.

Ether formation.

In general the most convenient method now known for forming the ethers of pentaerythritol is the reaction of pentaerythrityl tetrabromide with the sodium derivative of the alcohol or phenol, as described by Backer (10). Nichols and Yanovsky (11) have accomplished ether formation by the reaction of an alkyl halide with pentaerythritol in presence of alkali, and Glattfeld and Schneider (12) by the reaction of an alkyl halide with the sodium derivative of pentaerythritol in liquid ammonia.

Alkylation of pentaerythritol by splitting off water with other alcohols or with phenols appears to be unknown, although this is a familiar procedure for making ethers of aliphatic alcohols and of naphthols. It has even been patented by Dahlen, Black, and Foohey (13) as a way of preparing naphthyl ethers of glycols.

Amine formation.

Most of the N-substituted amines derived from pentaerythritol that are described in the literature have been prepared by reaction of a pentaerythrityl tetrahalide (generally the tetrabromide) with the desired amine. Alphen (14) has prepared secondary amines from pentaerythrityltetramine by condensation with aldehydes, followed by reduction of the products. In both cases pentaerythritol had to be converted first into the tetrahalide.

Formation of amines from pentaerythritol by splitting off water with primary amines has not been reported in the literature, although this is a well-known procedure for simpler alcohols, as in the alkylation of aniline by heating with methanol and acid.

Reaction of pentaerythritol with urea.

Simple alcohols react at their boiling points with urea to give urethanes. This suggests that the reaction of pentaerythritol with urea might give the corresponding urethane, which might be useful in Nylon-type fiber formation and in other plastics. However, Dittmar and Loder (15) obtained ethyleneurea and not the corresponding urethane by heating urea and ethylene glycol at 200-300° in a sealed tube. Degering (16) says that resinous materials are obtained by heating urea or its simple derivatives with alcohols or phenols in the presence of a catalyst and under pressure.

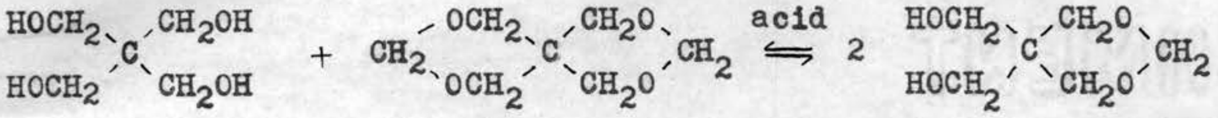
Preparation of tetrakis(mercaptomethyl)methane.

The tetrathio derivative of pentaerythritol has been prepared by Backer and Evenhuis (17) by the reduction of 2,3,7,8-tetrathiaspiro[4.4]nonane (obtained from pentaerythrityl tetrabromide and sodium tetrasulfide) with sodium in liquid ammonia, and treatment of the product with acid to decompose the sodium salt. Tetrakis(mercaptomethyl)methane has also been prepared by Farlow and Signaigo (18) from the polymeric product obtained by the action of sodium tetrasulfide in dioxane solution over a cobalt polysulfide catalyst. The tetramercaptan condenses with ketones, such as 1,4-cyclohexanedione, to give linear polymers suitable for bristles (19).

Both preparations are complicated and a simpler synthesis, such as described by Frank and Smith (20) for other alcohols, is desirable. They obtained several mercaptans in good yield by direct action of thiourea and hydrobromic acid on alcohols. The isothiouronium salts thus obtained were then decomposed with sodium hydroxide.

EXPERIMENTAL

(1) Preparation of the monoformal of pentaerythritol.



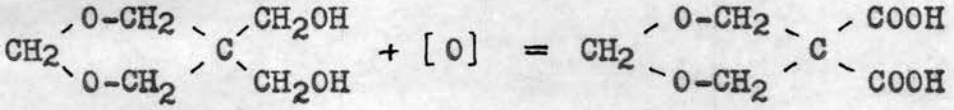
First run:

Pentaerythritol diformal was available as a research preparation from earlier work. This diformal (40 g., 0.25 mole), pentaerythritol (34 g., 0.25 mole), and 0.5 ml. of concentrated phosphoric acid (85%) were heated together under reflux for 2 hours in a 250-ml. round-bottomed flask to which an air-cooled condenser was attached. The yellow-brown solution was then distilled at a pressure of about 30 mm. Two fractions were obtained, one boiling at 150-180° and the other, a smaller fraction, at 210-230°. The latter was redistilled at high vacuum. However, after small amounts of the diformal had come over at 96-98°, bumping of the mixture, which had unaccountably become partly solid, made further distillation impossible.

Second run:

The diformal of pentaerythritol (60 g., 0.375 mole), pentaerythritol (51 g., 0.375 mole) and 85% phosphoric acid (0.5 ml.) were refluxed for 2 hours and then neutralized with the required amount of sodium hydroxide at a temperature of about 100°. The solution while still warm was placed in a Claisen distilling flask and distilled at a pressure of 0.25 mm. There were obtained 17.5 g. of the diformal, boiling at 92-100°, and 61 g. of the monoformal (55% of the theoretical amount), boiling at 150-152°. The melting point of the monoformal of pentaerythritol was 59° after one recrystallization from benzene; the literature value is 60° (19).

(2) <u>Oxidation and hydrolysis of the monoformal of pentaerythritol</u>.



The monoformal of pentaerythritol (14.8 g., 0.1 mole) was dissolved in 50 ml. of water containing 5 g. of sodium carbonate. Under mechanical stirring and cooling in an icebath to 4° a cold potassium permanganate solution (42.1 g. in 800 ml. of water) was slowly added. This is essentially the procedure of Fournier (21) for oxidizing primary alcohols to acids. After 12 hours of stirring the solution was filtered and then evaporated to dryness on a waterbath. The residue was acidified with 10% hydrochloric acid and dried again. The crystalline product consisted only of inorganic salts and did not contain any organic material.

The negative result could have been predicted after it was shown that even the <u>di</u>formal of pentaerythritol decolorizes a cold, alkaline solution of potassium permanganate. Potassium permanganate thus oxidizes not only the alcoholic groups of the monoformal, but also its ether linkages, the final oxidation products being carbon dioxide and water.

A solution of 5 g. of the monoformal of pentaerythritol in 150 ml. of a 5% sodium hydroxide solution was prepared and kept boiling for 3 hours. The cold, clear liquid was then neutralized with about 19 ml. of concentrated hydrochloric acid and evaporated to dryness on a waterbath. In order to find out whether any pentaerythritol had been formed, the crystals were dissolved in 20% hydrochloric acid and treated with benzaldehyde. No precipitate was formed. The same negative result was obtained with acid, benzaldehyde, and the monoformal, whereas a voluminous precipitate of the dibenzylidene derivative was formed with pentaerythritol. This proved that hydrolysis of the monoformal in alkaline solution did not take place.

(3) Esterification of pentaerythritol with methyl acrylate.

$$C(CH_2OH)_4 + 4\ CH_2{=}CHCOOCH_3 \overset{\text{cat.}}{\rightleftharpoons} C(CH_2OOCCH{=}CH_2)_4 + 4\ CH_3OH$$

Apparatus and procedure.

The alcoholysis was run according to Rehburg (7). The reagents were placed in a three-necked, round-bottomed 500-ml. flask having a glass tube in one neck by which to introduce carbon dioxide. The flask was equipped with a stirrer and attached to an eight-ball Snyder fractionating column which could be operated under total reflux. The reaction mixture was heated in an oil bath. An ordinary water condenser and an Erlenmeyer flask as a receiver completed the distilling apparatus. In order to have a measure of flow of the carbon dioxide, it was finally passed through a small beaker containing water. All the glass connections were kept air-tight in order to prevent air from getting into the apparatus, since this would cause polymerization not only of the product formed, but also of the methyl acrylate in the fractionating column and in the condenser during the distillation.

Methyl acrylate can be recovered from its methanol azeotrope by washing out the methanol with water. By measuring the distillate before and after addition of water the approximate amount of methanol was obtained. The two layers were then separated and the methyl acrylate dried with sodium sulfate. When the so recovered methyl acrylate was not used directly, a small amount of hydroquinone was added to prevent polymerization.

The fractionating column used was not efficient enough to produce the pure azeotrope of methyl acrylate and methanol which boils at $62-63^{\circ}$ (7). In order to obtain a boiling point as low as possible the oil bath temperature had to be kept low, the amount of carbon dioxide passing through the reaction mixture small, and the speed of the stirrer only so fast as to prevent the insoluble pentaerythritol from collecting at the bottom of the flask. Even when distillation was slow, the applied excess of methyl acrylate was not always enough to complete the reaction. In this case methyl acrylate was added during the reaction.

After the distillation 250 ml. of cold water were added to the brown residue, which dissolved wholly. Sodium bicarbonate was added until the solution was neutral and no carbon dioxide evolved any more. The solution was then extracted twice with 600 ml. of ether, washed with water, and dried with anhydrous sodium sulfate. After evaporation of the ether, small amounts of methyl acrylate were distilled off, reduced pressure being used in order to keep the temperature low and so to prevent polymerization. The color of the oily product thus obtained, which still contained hydroquinone, was reddish-brown.

The melting point of the pentaerythritol tetraacrylate was expected to be between 0° and 100°, the melting point of the tetraacetate being 84-86° and that of the tetrapropionate being 25-30° (19). The boiling point can be assumed to be between 150° and 200° at 1-2 mm. pressure, the boiling points of the tetraacetate and tetrapropionate being 155-160° and 170-175° respectively at 2 mm. pressure (19).

Both recrystallization and distillation at low pressure were attempted without success.

<u>First run</u>.

Amount of reagents applied:

17 g. (0.125 mole) of crude pentaerythritol (from Cities Service Research Laboratory, Tallant, Okla.)

86 g. (1 mole) of methyl acrylate (EKC practical)

5 g. of hydroquinone

1 ml. of concentrated sulfuric acid

The oil bath was heated to 105° and the reaction mixture kept under total reflux for 2 hours. Even at the beginning of the distillation the color of the reaction mixture changed from white to brown and the formation of a small amount of resinous products could be observed. Although no stirring was employed in this first run, 5 g. of methanol (31% of the theoretical amount) were collected, which proved that alcoholysis took place. The boiling point was 70° at the beginning of the distillation and increased until it was 76° at the end of 6 hours (boiling point of methyl acrylate: 80°).

Second run:

Amount of reagents applied:

34 g. (0.25 mole) of crude pentaerythritol
258 g. (3 moles) of methyl acrylate
12 g. of hydroquinone
1.5 ml. of concentrated sulfuric acid

Reflux time	2 hours
Distilling time	7 hours
Distilling temperature	71-74°
Oil bath temperature	100°
Amount of methanol collected	27.6 g. (86% of the theoretical amount)

The reddish-brown oil was distilled in a 25-ml. distilling flask at a pressure of 0.4 mm. in an atmosphere of nitrogen. When the oil bath temperature reached 190° the contents of the flask became solid within a few seconds and the distillation had to be discontinued.

Third run:

The same amount of reagents and the same conditions as described above were applied.

Distillation yielded 26.7 g. of methanol, which corresponds to 83% of the theoretical yield. After neutralization, extraction and evaporation of the solvent 54 g. (51% of the theoretical amount) of a dark-red oil were obtained, still containing hydroquinone. Addition of picric acid as an inhibitor led to the formation of violet crystals, which were insoluble in ether and could not be distilled.

High-vacuum distillation at 0.3 mm. pressure and under carbon dioxide atmosphere again had to be stopped at an oil bath temperature of 185° because of polymerization.

Fourth run:

In order to prevent side reactions, such as oxidation and addition of sulfuric acid to the carbon-carbon double bond of the acrylate radical, another catalyst, m-nitrobenzenesulfonic acid, was used and the crude pentaerythritol was replaced by pure pentaerythritol (EKC white label).

Amount of catalyst	2 g.
Reflux time	1 hour
Distilling time	8 hours

Only 8 g. of methanol (25% of the theoretical amount) were collected. This poor result suggests that m-nitrobenzenesulfonic acid was not effective enough as catalyst.

Fifth run:

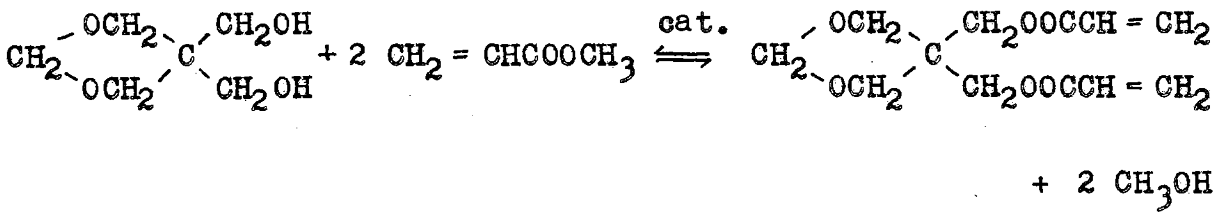
Pure pentaerythritol was used, and concentrated sulfuric acid was again used as catalyst, but in smaller quantity (1 ml. instead of 1.5 ml.). The distilling temperature was higher (75-77°) than in the other runs and only a very small amount of methanol was collected. Addition of sulfuric acid after 3 hours of distillation did not increase the amount of methanol. After 9 hours of distillation only 15.2 g. of methanol had distilled over (47.5% of the theoretical amount), although the conditions were almost the same as for the earlier runs. Again the red product obtained did not contain any solid material. It was purified by boiling the alcoholic, neutralized solution with charcoal. After filtration and evaporation of the alcohol a yellow oil was obtained, which was insoluble in ether and benzene, and soluble in ethyl and methyl alcohol. Attempts at crystallization from ethanol-water, methanol-water and ethanol-benzene were without success.

The oil probably consisted of a mixture of the mono-, di- and triacrylates (the diester prevailing). Since the boiling point of the diester may be expected to be very high, even a high-vacuum distillation would probably fail.

Sixth run:

Sodium methoxide was used as catalyst. About 0.5 g. of sodium were dissolved in 10 ml. of absolute methanol and added to the usual reaction mixture of ester, pentaerythritol, and inhibitor. After it had been kept under reflux for 1½ hours, distillation was started. Only 8 ml. of methanol were collected at the beginning of the distillation. After the first 80 ml. had distilled, the boiling point stayed at 78° and no further methanol could be collected. After 3 hours the solution was therefore acidified with 1.5 ml. 85% phosphoric acid and the distillation was kept going for another 4½ hours. No methanol was obtained. The mixture was neutralized and filtered. The crystalline residue weighing 36 g. was insoluble in ether (34 g. of pentaerythritol and 2 g. of sodium salts). It was concluded that alcoholysis did not take place.

(4) Esterification of the monoformal of pentaerythritol with methyl acrylate.



Amounts of reagents applied:

29.6 g. (0.2 mole) of the monoformal

260 g. (3 moles) of methyl acrylate

10 g. of hydroquinone

1 g. of sodium methoxide

Reflux time	1 hour
Distilling time	2 hours

No methanol distilled over except for the few milliliters that were added with the sodium methoxide. The yellow reaction mixture was therefore acidified with 1.5 ml. of concentrated sulfuric acid. The color soon changed to a dark brown. After 3 hours of further distillation the reaction was stopped, because no methanol distilled over.

(5) Ether formation between pentaerythritol and isopropyl alcohol.

$$C(CH_2OH)_4 + 4\ (CH_3)_2CHOH \overset{\text{acid}}{=} C[CH_2OCH(CH_3)_2]_4 + 4\ H_2O$$

Pentaerythritol (13.6 g., 0.1 mole), isopropyl alcohol (130 ml.) and concentrated sulfuric acid (25 ml.) were refluxed together for 3 hours. The solution stayed absolutely clear and colorless. Only small amounts of propylene escaped. After addition of 25 ml. of sulfuric acid, the boiling was continued. Large amounts of propylene were formed and the color soon changed to a dark red. After 3/4 hour of boiling the reaction mixture, which formed two layers, was cooled, diluted with 250 ml. of water, and extracted with ether. A dark liquid (5 ml.) with a strong odor suggesting the presence of sulfur was obtained. Charcoal treatment and refluxing with 5% sodium hydroxide solution did not change that odor.

(6) Ether formation between pentaerythritol and

(a) phenol:

$$C(CH_2OH)_4 + 4\ C_6H_5OH \overset{\text{acid}}{=} C(CH_2OC_6H_5)_4 + 4\ H_2O$$

Phenol (140 g.) and concentrated sulfuric acid (1 ml.) were heated to 150° and kept at that temperature for 20 minutes. After addition of 13.6 g. (0.1 mole) of pentaerythritol the resulting clear solution was kept boiling for 4 hours. After this time 3 ml. of water were removed by distillation. The boiling was continued another 7½ hours, after which time another 3 ml. of water were distilled.

The dark solution was extracted with 300 ml. of benzene and washed with 60 g. of sodium hydroxide in 400 ml. of water. The benzene solution, which showed a yellow fluorescence, became almost colorless after refluxing it with charcoal for 20 minutes. After evaporation of the solvent, crystallization of the residual oil from benzene-petroleum ether was attempted, but in vain.

(b) <u>2-naphthol</u>:

$$C(CH_2OH)_4 + 4\ C_{10}H_7OH \overset{\text{acid}}{=} C(CH_2OC_{10}H_7)_4 + 4\ H_2O$$

In order to form a sulfonic acid to serve as a catalyst, 100 ml. of xylene (commercial mixture) were boiled for 10 minutes with 1 ml. of concentrated sulfuric acid. Addition of 6.8 g. (0.05 mole) of pentaerythritol and 28.8 g. (0.2 mole) of 2-naphthol gave a clear, dark solution. After boiling under reflux for 1 hour the amount of water formed was measured by distilling it into a graduated cylinder. The 3 ml. of water collected represented 83% of the theoretical amount.

The dark solution was extracted with ether, thoroughly washed with 10% sodium hydroxide solution, neutralized by washing repeatedly with water, and dried with anhydrous sodium sulfate. The brown solution showed a strong, green fluorescence. After evaporating the ether, slightly brown crystals were obtained from the cold xylene solution. After refluxing with charcoal in toluene and recrystallization the white crystals weighed 13.8 g. (43% of the theoretical amount). Their melting point was 150-154°. They were soluble in ether, alcohol, chloroform, acetone, benzene, hot toluene, hot xylene, and glacial acetic acid, but insoluble in acids, bases, and low-boiling petroleum ether.

Melting points after recrystallization from benzene-petroleum ether:

three times:	156.5-157.5°
five times:	158-159°
seven times:	158-159°

A sample of the product, which had been recrystallized seven times, was analyzed.

Result:

	C	H
	81.99%	6.50%
	82.09%	6.43%

Calculated values for the several expected 2-naphthyl ethers of pentaerythritol:

tetraether	84.3%	5.63%
triether	81.7%	5.83%
diether	77.3%	6.18%
monoether	68.7%	6.87%

The results show that the analyzed sample was not one of the four ethers nor a mixture of them.

A sample of the crude product was purified by making the picrate: 2.3 g. of picric acid dissolved in hot glacial acetic acid were added to a hot, saturated solution of 3.2 g. of the product in glacial acetic acid. Orange crystals melting at 167-170° were obtained upon cooling. After recrystallization from absolute alcohol (melting point 172-173°) the picrate was dissolved in glacial acetic acid and water was added to the boiling solution. The obtained oil was recrystallized from toluene. The melting point of the white crystals was 157.5-158.5°.

It was obvious that the product obtained was not the expected ether. Nevertheless two attempts were made to duplicate the preparation. Another product, recrystallizable from benzene and melting at 130-132° in the unpurified state, was obtained both times. It was soluble in alcohol.

Melting points after recrystallization from benzene:

once	130-132°
twice	145-146°
three times	146-146.5°
five times	146.5-147°
six times	146.5-147°

Mixed m.p. with product melting at 158-159°: 130-145°.

A sample of the purified product was recrystallized three times from acetone-petroleum ether instead of benzene. The melting point was the same and a mixed melting point with the original did not show any depression.

In order to find out whether the solvent took part in the reaction the solvent was changed. The reaction was run twice in ethylbenzene as solvent, this being chosen because it has almost the same boiling point as xylene and is otherwise similar to it. A white, crystalline product was obtained both times melting at 168-171° in the unpurified state, soluble in benzene and recrystallizable from alcohol-water.

Melting points after recrystallization from alcohol-water:

once	168-171°
twice	172-172.5°
three times	172.5-173°
four times	172.5-173°
five times	172.5-173°

Mixed m.p. with product melting at 158-159°: 136-141°

Mixed m.p. with product melting at 146.5-147°: 126-145°

M.p. after three recrystallizations from acetone-ligroin: 172.5-173°.

In order to be certain that the pentaerythritol took part in the reaction a trial run was made without pentaerythritol. Boiling 2-naphthol in ethylbenzene with sulfuric acid as catalyst resulted in the formation of 2-naphthyl ether, recrystallizable from alcohol and melting at 105° (22).

To complete the series of trials pentaerythritol was heated together with ethylbenzene and sulfuric acid without the presence of 2-naphthol. No product was obtained.

None of the three different products obtained contained sulfur, nor decolorized a cold potassium permanganate solution.

The two new compounds, one melting at 146.5 - 147° and the other at 172.5 - 173°, were also analyzed. The following table gives the results and a tabular comparison of the three products.

% C	% H	Solv.	M.p.	Cryst.from	Sol. in	Cryst. Form
81.99 82.09	6.50 6.43	xylene	158-59°	benzene-ligroin	alcohol, benzene	cotton-like, needles
77.85 77.30	6.72 6.53	xylene	146.5-47°	benzene	alcohol	cotton-like, needles
89.25 89.05	5.93 5.75	ethylbenzene	172.5-73°	alcohol	benzene	flat cryst., no needles

(7) Reaction of pentaerythritol with aniline or aniline hydrochloride to give tetrakis(phenylaminomethyl)methane.

$$C(CH_2OH)_4 + 4\ C_6H_5NH_2 \overset{cat.}{=} C(CH_2NHC_6H_5)_4 + 4\ H_2O$$

First run:

Pentaerythritol (13.6 g., 0.1 mole), aniline (100 g.) and aniline hydrochloride as a catalyst (1 g.) were heated to boiling in a 200-ml. flask equipped with an air-cooled condenser. Even after 10 hours of boiling no water was formed, showing that no reaction took place.

Second run:

The same reaction was tried with anhydrous zinc chloride as catalyst. The result was again negative.

Third run:

Pentaerythritol (13.6 g., 0.1 mole) and freshly distilled aniline hydrochloride (51.8 g., 0.4 mole) were thoroughly mixed and heated to boiling. A clear, yellow solution was obtained which got darker during the course of the reaction. As soon as water began to appear in the reflux air-condenser, the latter was removed and the water formed was collected in a graduated cylinder. Within 45 minutes 6 ml. of a yellow, acid solution distilled over, whereupon the heating was stopped and the now brown solution cooled. The distilled liquid was made basic with sodium hydroxide to give two layers, one containing water and sodium chloride and the other (2 ml.) being aniline. The water formed during the reaction (7 ml.) corresponds to the theoretical amount.

The solid cake was dissolved in 300 ml. of water and 50 ml. of 10% hydrochloric acid and filtered from a small amount of tar. The acid, red, clear solution was placed in a 1 l. long-necked flask, neutralized with 15 g. of sodium hydroxide, and freed from aniline by steam distillation.

The organic, black layer was separated from the water layer and extracted with ether. Only a small amount was soluble in ether, the rest being insoluble tar. The red ether solution was neutralized by washing with water and dried with anhydrous sodium sulfate. The ether was evaporated after addition of alcohol, kept boiling with charcoal for 15 minutes, filtered, and cooled. After removing the alcohol an orange oil was obtained which was soluble in ether, alcohol, benzene and acetone, and insoluble in water and low-boiling petroleum ether. Attempts to get it into crystalline form from acetone-petroleum ether, benzene-petroleum ether and alcohol-water were without success.

The orange oil was therefore distilled under a pressure of 3 mm. and at a temperature of 210-230°. It was not possible to crystallize the distillate which probably still represented a mixture of difficultly separable amines.

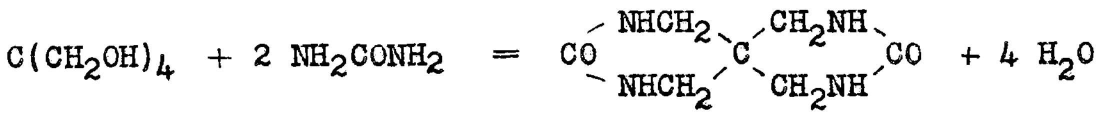
The same reaction was run again with the difference that an excess of aniline hydrochloride was used. The reaction temperature was not allowed to exceed 230° and the heating was stopped after 20 minutes, when the color of the reaction mixture was still yellow, in order to prevent formation of tar.

It was again impossible to crystallize the red oil which was obtained by the treatment described.

(8) <u>Reaction of pentaerythritol with urea</u>.

$$C(CH_2OH)_4 + 4\ NH_2CONH_2 = C(CH_2OCONH_2)_4 + 4\ NH_3$$

or



$$C(CH_2OH)_4 + 2\ NH_2CONH_2 = CO\begin{matrix}NHCH_2\\NHCH_2\end{matrix}C\begin{matrix}CH_2NH\\CH_2NH\end{matrix}CO + 4\ H_2O$$

Pentaerythritol (13.6 g., 0.1 mole) and urea (24 g., 0.4 mole) were heated in a sealed tube for 5 hours at 200°. The temperature was then increased to 230° within one hour and kept at 230° for another hour.

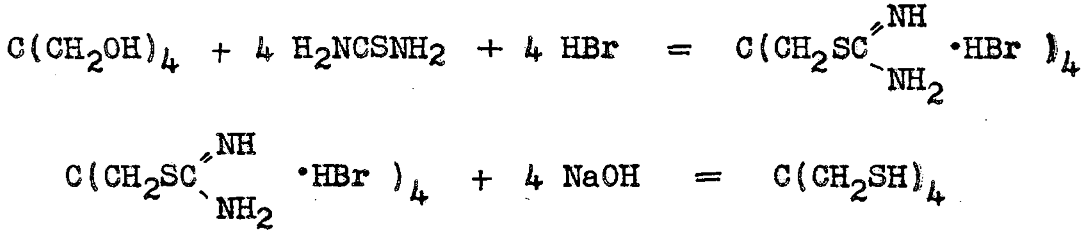
The same heating was applied to another sealed tube containing half of the amounts described.

The crystalline, yellow mixtures were dissolved in hot water and the water evaporated until crystallization occurred upon cooling. The long, white needles, which were very soluble in water and only slightly soluble in ether, alcohol and chloroform, gave the following melting points:

M.p. of X	185-190°
M.p. of urea	132-133°
Mixed m.p. of X with urea	112-113°
M.p. of X after recrystallization from hot water (3 times)	231-245°

The crystals gave a positive test for hydroxyl groups and the benzaldehyde test for pentaerythritol was strongly positive. They therefore represented a mixture of pentaerythritol and an unknown substance which was probably slightly more soluble in water than pentaerythritol. Fractional crystallization in such a way that the mother liquid was concentrated did not give a reasonable separation. The obtained melting point of 180-230° showed that pentaerythritol was still present.

(9) Conversion of pentaerythritol into the corresponding mercaptan by reaction with thiourea and hydrobromic acid.



$$C(CH_2OH)_4 + 4\ H_2NCSNH_2 + 4\ HBr = C(CH_2SC\genfrac{}{}{0pt}{}{\nearrow NH}{\searrow NH_2}\cdot HBr)_4$$

$$C(CH_2SC\genfrac{}{}{0pt}{}{\nearrow NH}{\searrow NH_2}\cdot HBr)_4 + 4\ NaOH = C(CH_2SH)_4$$

Pentaerythritol (13.6 g., 0.1 mole), thiourea (30.4 g., 0.4 mole) and 48% hydrobromic acid (200 g., 1.2 moles) were placed in a 500-ml. three-necked flask equipped with stirrer and reflux condenser. The clear, colorless solution was refluxed for 9 hours at an oil bath temperature of 135°. The solution was then made slightly basic by addition of 48 g. of sodium hydroxide in 400 ml. of water and refluxed for another 2 hours under a natural-gas atmosphere.

The yellow solution was filtered from a small amount of a dark-green precipitate which was insoluble in water and ether. After acidification with 2 ml. of concentrated hydrochloric acid and extraction with twice 200 ml. of ether the solution was washed with water and dried with anhydrous sodium sulfate. No residue was obtained after evaporation of the solvent.

DISCUSSION OF RESULTS

Preparation of the monoformal.

In order to increase the yield it was necessary to neutralize the reaction mixture before the distillation. The poor yield of monoformal by distillation with the acid catalyst present may be due to disproportionation of the monoformal into the diformal and pentaerythritol as soon as the diformal, which has the lower boiling point, distills over. Separation by distillation seems to be much better than fractional crystallization because the solubility difference in hot benzene is only small and because both the diformal and the monoformal are hygroscopic.

The positive result suggests that it is possible to prepare the monoformal by reacting 1 mole of pentaerythritol with 1 mole of formaldehyde (or perhaps an excess) in the presence of phosphoric acid as catalyst and separating the diformal and monoformal formed by fractional distillation.

Oxidation and hydrolysis of the monoformal.

Although hydrolysis of the monoformal, as expected, does not take place in alkaline medium, the ether linkages of the monoformal are oxidized by a cold, alkaline solution of potassium permanganate. The failure of the oxidation to yield the desired product may be compared to that of the diacetone compound of tetrahydro-3,3,5,5-tetrakis(hydroxymethyl)-4-pyranol to give the corresponding 4-pyranone (23) upon oxidation with either permanganate or the theoretical amount of chromic acid in glacial acetic acid. On the other hand, diacetonesorbose can be oxidized with potassium permanganate to diacetoneketogulonic acid according to a Dutch patent (synthesis of l-ascorbic acid) (24).

Esterification of pentaerythritol with methyl acrylate.

Although it was not possible to obtain the tetraacrylic ester of pentaerythritol in the pure state, the formation of about the theoretical amount of methanol proves that esterification took place. Separation and purification of the residue by high-vacuum distillation under carbon dioxide or nitrogen atmosphere did not succeed, the contents of the distilling flask being polymerized at 190°. Moreover, there does not appear to be any other successful way of purification, since a fractional crystallization of different esters, the solubilities and melting points of which are unknown, is rather unlikely to succeed.

Despite the fact that sulfuric acid gives side products, it seems to be the best catalyst, phosphoric acid, m-nitrobenzenesulfonic acid and sodium methoxide being ineffective.

Pure pentaerythritol did not react as well as crude pentaerythritol did, which might be explained by a catalytic effect of the impurities of the crude pentaerythritol.

Ether formation between pentaerythritol and isopropyl alcohol.

In order to make the pentaerythritol react with isopropyl alcohol the amount of concentrated sulfuric acid as condensing agent had to be so large (10 moles of sulfuric acid to 1 mole of pentaerythritol) that the formation of propylene became the main reaction and only a small amount of other products, which furthermore contained sulfur, were obtained.

Ether formation between pentaerythritol and phenol.

The formation of water proves that pentaerythritol reacted in some way or other. Whether the residual oil represented the tetraphenyl ether of pentaerythritol is doubtful considering the results obtained with pentaerythritol and 2-naphthol.

Ether formation between pentaerythritol and 2-naphthol.

Three different crystalline products have been obtained, none of them being a simple ether between pentaerythritol and 2-naphthol or representing a mixture of different simple ethers between pentaerythritol and 2-naphthol. At least two of the three products can be assumed to be pure, single compounds, since their preparation can be duplicated and since recrystallization from different solvents does not change their melting points.

It has been proved that at least one of the solvents, xylene or ethylbenzene, takes part in the reaction, because the product formed with xylene as solvent is different from the one formed with ethylbenzene as solvent, although both solvents have practically the same boiling point and other physical characteristics. It is obvious that the constitution of the two products is quite different, their melting point difference being 25° and their crystalline forms and solubilities being entirely different. A desirable further experiment to establish whether both aromatic solvents participate would be to effect the reaction in a truly nonreactive solvent; ethylcyclohexane should be satisfactory.

The fact that no product is formed in the absence of 2-naphthol shows that the solvent does not react with pentaerythritol. It has been proved furthermore, that pentaerythritol, or at least a fragment of it, takes part in the reaction, since only 2-naphthyl ether is formed in the absence of pentaerythritol. The latter reaction shows also that the solvent does not react with 2-naphthol.

It becomes almost certain that pentaerythritol does not take part as such in the reaction, since the solvent does not react with pentaerythritol nor with 2-naphthol in the absence of the third component, although it has been proved that the solvent participates.

Under the conditions applied pentaerythritol might decompose into formaldehyde, acetaldehyde, methanol and methylacrolein, thus complicating the reaction considerably (24).

In spite of much speculation, it has not been possible to establish any configuration of the products which would be in agreement with the carbon-hydrogen analysis. It can only be said that the products obtained, which do not contain any sulfur, are of the nature of ethers, containing at least one naphthyl radical and one ethylbenzene or xylene radical.

Reaction of pentaerythritol with aniline or aniline hydrochloride.

Both catalysts, aniline hydrochloride and zinc chloride, are ineffective. The water formed by refluxing pentaerythritol and aniline hydrochloride shows that a reaction took place. However, the oil obtained could be purified neither by distillation nor by crystallization. It probably represented a mixture of difficultly separable amines.

Reaction of pentaerythritol with urea.

The melting point of the product obtained and its crystalline form show that a new product was formed. Pentaerythritol alone never crystallizes in long needles, and the solubility of urea in water is so high that the product could not have represented mixed crystals between pentaerythritol and urea. However, the solubility properties of the reaction product were so close to those of pentaerythritol itself that a separation could not be attained.

Preparation of the tetramercaptan of pentaerythritol.

The negative result is not so astonishing, if it is realized that this reaction (like the direct preparation of the tetrahalides) unavoidably requires the loss of the hydroxyl groups, which is much more difficult to accomplish for a neopentyl-type alcohol like pentaerythritol.

Another reaction that seems to be worth while investigating is the direct synthesis of pentaerythritol tetrahalides (especially the tetrachloride) by reaction of pentaerythritol with halogen acids in a high boiling solvent, such as nitrobenzene or pyridine.

SUMMARY

1. Pentaerythritol monoformal has been prepared by the equilibration of pentaerythritol and its diformal, and effectively purified by distillation. It resists alkaline hydrolysis, but is destroyed by alkaline permanganate oxidation.

2. Conversion of pentaerythritol to its tetraacrylate succeeded, but the product polymerized during purification. Related conversions to polyamines (with aniline) and polyamides (with urea) gave evidence of succeeding, but the products could not be purified, most likely because of their similar, polyfunctional nature.

3. Whereas pentaerythritol and phenol gave no solid derivatives, the use of 2-naphthol in aromatic hydrocarbon solvents produced at least two new crystalline compounds. Unfortunately the participation of the solvent and probable fragmentation of the pentaerythritol made the products so complex that no reasonable structures have been devised to fit their analyses.

4. Pentaerythritol, behaving as a neopentyl alcohol rather than as an ordinary primary alcohol, cannot be converted to the corresponding tetra-thiol with hydrobromic acid and thiourea by the method of Frank and Smith.

BIOGRAPHY

Otto Sturzenegger was born at Zurich, Switzerland, February 27, 1926. After completing his grade school and high school training in Zurich he enrolled in the Federal Institute of Technology in Zurich where he received the degree of a Chemical Engineer in August of 1948. An exchange scholarship made it possible for him to come to the United States where he entered the Graduate School of Oklahoma A. and M. College to do graduate work in the Department of Chemistry.

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