

THE CHEMICAL REACTIONS OF PENTAERYTHRITOL AND ITS DERIVATIVES

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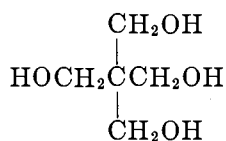
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I. INTRODUCTION

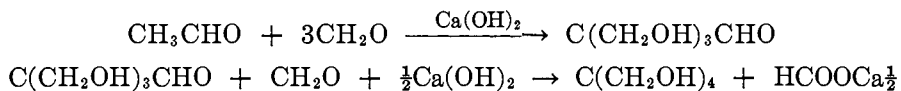
Pentaerythritol, or tetramethylolmethane, is the tetrahydric alcohol



and when pure is a colorless crystalline material melting without decomposition at 263°C. It can be sublimed under reduced pressure (58). It is soluble in about 18 parts of water at 15°C., and can be recrystallized readily from hot water. It is also soluble to some extent in alcohol, acetone, dioxane, pyridine, and liquid ammonia.

Pentaerythritol was first prepared by Tollens and Wigand (146) in 1891 by

the action of formaldehyde on acetaldehyde in the presence of lime. Many modifications of the reaction have been reported in the patent literature, but essentially the same reaction is used today for the commercial production of pentaerythritol. A process in which caustic soda replaces the lime is also in operation commercially. The reaction takes place in one operation, but it can be represented as taking place in two stages:



Pentaerythritol has been manufactured in large quantities during the last few years for conversion to its explosive tetranitrate. It has also a large potential market as a component in resinous compositions.

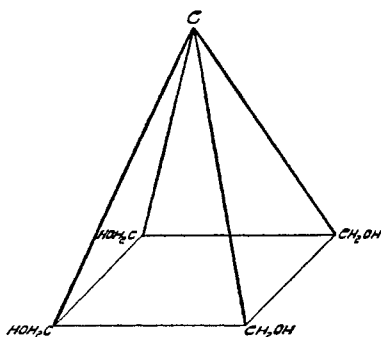


FIG. 1

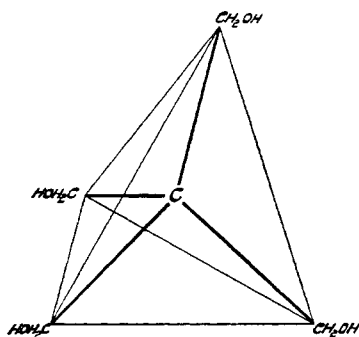


FIG. 2

This review is concerned only with the chemical reactions undergone by pentaerythritol and its derivatives which give non-polymeric products. The known derivatives of pentaerythritol have been tabulated and their melting and boiling points are listed. The indexes of *Chemical Abstracts* have been searched up to 1946 and references uncovered during general reading in 1947 are included.

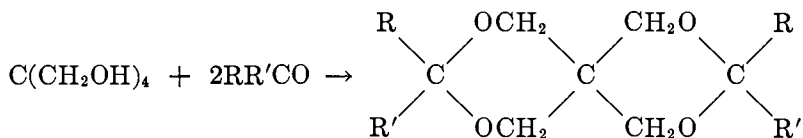
II. CONFIGURATION

Early work on x-ray examinations of the crystal structure of pentaerythritol by Mark and Weissenberg (104) and Huggins and Hendricks (85) seemed to point to a pyramidal grouping of the four CH_2OH groups around the central carbon atom (figure 1) in place of the generally accepted tetrahedral distribution (figure 2), and work on the external symmetry of the crystals by Westbrink and van Melle (151) and by Giebe and Scheibe (65) was supposed to confirm this.

However Mark and Weissenberg, and Huggins and Hendricks, accepted the class C_{4v} originally given by Martin (105), being unaware that Haga and Jaeger (81) had shown by means of a Laue photograph that the planes of symmetry supposed to intersect in the tetrad axis were non-existent. The C_{4v} class was therefore unacceptable and various papers on this point followed.

Armed with the evidence of Liebisch (95) that the pyroelectric test gave positive results for the crystals, and of Giebe and Scheibe (65) that a positive result was obtained for the piezoelectric test, Weissenberg (150) and Reis (128) developed a new stereochemistry for the carbon atom, based on its possible non-tetrahedral form. Nitta (117) and Hendricks (83) repeated the x-ray investigation and showed that the results were consistent with either a pyramidal (C_4) or a sphenoidal (S_4) symmetry of the pentaerythritol molecule. A number of publications on the crystallographic aspects of the problem were presented at about this time and the literature up to 1928 was summarized by K. Lonsdale (98). Further studies by, for example, Knaggs (90), Möller and Reis (108), Mark and Susich (103), and Llewellyn, Cox, and Goodwin (97) of pentaerythritol and its derivatives finally agreed upon a tetrahedral configuration about the central carbon atom. Raman spectrum analysis (112) and dipole moment measurements were also found to favor the tetrahedral configuration (139).

An attempt was made by Böeseken and Felix (31, 32, 33) to decide between the tetrahedral and pyramidal configurations for pentaerythritol chemically, by forming spirocyclic compounds by condensation with aldehydes or ketones and attempting to resolve them.



If the configuration is tetrahedral, the acetal or ketal must be dissymmetric and capable of resolution, but if it is pyramidal, *cis-trans* isomerism would be encountered. Read (127) had previously prepared compounds of this type and had made unsuccessful attempts to resolve them.

Böeseken and Felix prepared the spirocyclic ketal from ethyl pyruvate, and after hydrolysis of the ester grouping were able to resolve the resulting acid in the normal manner with strychnine. In another experiment the dibenzylidene derivative was obtained in optically active forms by spontaneous resolution of the racemate, but this could not be repeated.

The resolution, as was pointed out by Senezov (137), does not by itself establish the tetrahedral structure of pentaerythritol, since on examination the *trans* form of the pyramidal molecule of the condensation product is seen to be dissymmetric. It has been suggested also, by Kenner (89), that chemical methods are not suitable for testing the validity of Weissenberg's principle, owing to the possibility of transformation to a tetrahedral configuration during reaction. Böeseken and Felix maintained that the enantiomorphs of the pyramidal type would be so labile as to render their isolation impossible. The accomplished resolution of the sole reaction product, together with the failure to detect any trace of *cis-trans* isomers, may therefore be taken as evidence in favor of the tetrahedral configuration.

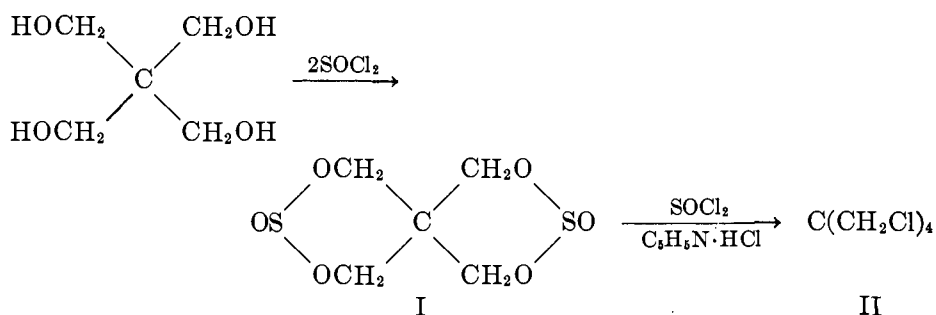
Orthner and Freyss (119) have put forward suggestions on the spatial arrangement of the groups in the pentaerythritol molecule, based on the fact that where-

as pentaerythritol gives an increase of specific conductivity in boric acid solution, disubstituted pentaerythritol derivatives, such as the dimethyl ether and dibenzoate, give no increase.

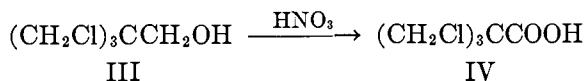
III. HALIDES

A. Chlorides

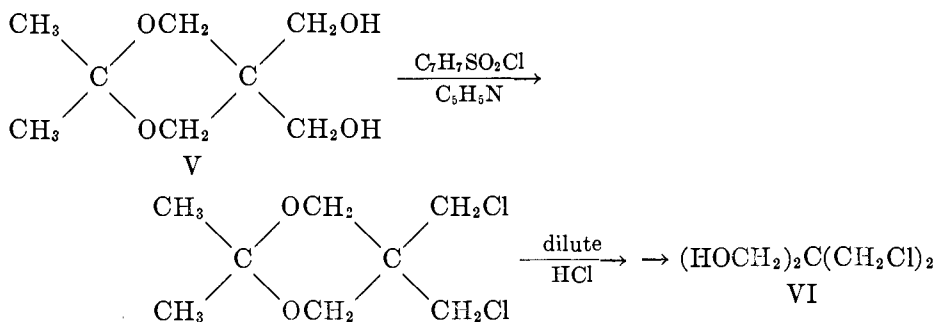
Fecht (56), in 1907, first reported that the action of concentrated hydrochloric acid on pentaerythritol at 120–180°C. gave a mixture of mono-, di-, and tri-chloro derivatives. He converted the trichloride to the tetrachloride by reaction with phosphorus trichloride at 150°C. The tetrachloride (II) has been prepared by Govaert, Hansens, and Beyaert (77) by the reaction of pentaerythritol with thionyl chloride to give the disulfite (I), followed by further reaction of this with thionyl chloride in the presence of a pyridine hydrochloride catalyst.



Mooradian and Cloke (109) have used substantially the same method for the preparation of the tetrachloride, and of mixtures of the chlorides in which either the dichloride or trichloride can be made to predominate. Their reaction is carried out in pyridine solution without intermediate isolation of the disulfite. The same authors have found that pentaerythrityl trichloride (III) is readily oxidized by nitric acid to give the corresponding trichloropivalic acid (IV).



Rapoport (125) has prepared pentaerythrityl dichloride (VI) uncontaminated



with other chloro derivatives by the action of *p*-toluenesulfonyl chloride on the monoisopropylidene derivative of pentaerythritol [2,2-dimethyl-5,5-bis(hydroxymethyl)-1,3-dioxane (V)] in the presence of pyridine, followed by opening of the dioxane ring with dilute hydrochloric acid.

The preparation of pentaerythrityl dichloride from pentaerythritol and sulfur monochloride has also been reported by Bougault (35), but his product was impure.

The pentaerythrityl chlorides and their simple derivatives are listed in table 1.

TABLE 1
Pentaerythrityl chlorides

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
$C(CH_2Cl)_4$	97	110/12 mm.; 110/12 mm.	(56, 77, 109)
$(CH_2Cl)_3CCH_2OH$	65.5 (80)	127.5-129/12 mm. (136/12 mm.)	(109) (56)
$(CH_2Cl)_2C(CH_2OH)_2$	83 (95; 65)	158.5-160/12 mm.	(56, 109) (35)
$\begin{array}{c} CH_2O \\ / \quad \backslash \\ (CH_2Cl)_2C \quad C(CH_3)_2 \\ \backslash \quad / \\ CH_2O \end{array}$	48-49		(125)
$(CH_2Cl)_2C(CH_2ONO_2)_2$			(152)
$CH_2ClC(CH_2OH)_3$	141	190/12 mm. 183-188/16 mm.	(56) (109)
$CH_2ClC(CH_2ONO_2)_3$			(152)

B. Bromides

The pentaerythrityl bromides are probably the most important halides of pentaerythritol, as they are employed most frequently as starting products for the preparation of the other pentaerythritol derivatives.

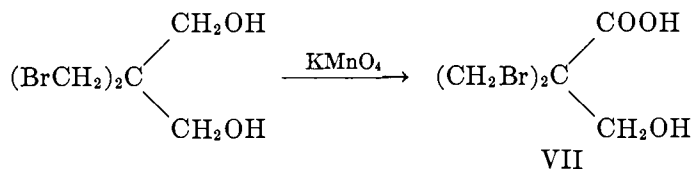
Beyaert and Hansens (27) have reported a convenient method for the preparation of pentaerythrityl mono- and di-bromides, involving the reaction of pentaerythritol and hydrogen bromide in glacial acetic acid followed by saponification of the bromoacetates formed. With varying proportions of hydrogen bromide a 65 per cent yield of the monobromide together with 16 per cent of the dibromide, and an 80 per cent yield of the dibromide together with 18.5 per cent of the tribromide, were obtained. The monobromide has also been isolated by fractional distillation at 1 mm. of the mother liquors from the preparation of

the dibromide (68). Barbieri and Matti (21) have prepared a mixture of the mono- and di-bromides by reaction of pentaerythritol with aqueous hydrobromic acid at 120°C. Zelinski (157) recorded the preparation of the dibromide by heating pentaerythritol and aqueous hydrobromic acid together at 125°C.; however, Bincer and Hess (28) found that by this method there is also formed a considerable proportion of the tribromide.

Hansens and Beyaert (82) have found that the tribromide is best prepared by the method of Perkin and Simonsen (121), which involves the treatment of pentaerythritol with hydrogen bromide in glacial acetic acid at 165°C. Perkin and Simonsen state that this reaction gives a mixture of the tetrabromide and the tribromide monoacetate, but state no yields. Hansens and Beyaert record a 96 per cent yield for the tribromide. Bincer and Hess (28) have prepared the tribromide from pentaerythritol and hydrobromic acid at 140°C., and Rave and Tollens (126) obtained a mixture of the tri- and tetra-bromides by the reaction of pentaerythritol with phosphorus tribromide at 100–150°C.

Schurink has reported that pentaerythrityl tetrabromide can be prepared conveniently in 86 per cent yield, without the use of a pressure vessel, by the reaction of pentaerythritol with phosphorus tribromide at an elevated temperature (15, 135). The preparation of this compound has also been reported by numerous other workers (60, 78, 82, 121, 126). Perkin and Simonsen (121) recorded the surprising unreactivity of the tetrabromide and attributed this in some degree to its insolubility. Dostrovsky, Hughes, and Ingold (48) point out that as pentaerythrityl tetrabromide is a substituted neopentyl bromide, its bimolecular substitutions are of necessity sterically hindered.

Glattfeld and Schneider (67) have oxidized pentaerythrityl dibromide with permanganate, and obtained the monobasic acid 1,1-bis(bromomethyl)-2-hydroxypropionic acid (VII).



The pentaerythrityl bromides and their derivatives are listed in table 2.

C. Iodides

Pentaerythrityl monoiodide has only been prepared as a by-product; it was isolated by Govaert and Beyaert (68) from the mother liquors from the preparation of the diiodide, by fractional distillation at 1 mm.

The diiodide has been prepared by Tollens and Wigand (146) by the reaction of pentaerythritol with hydriodic acid and red phosphorus at 170–180°C.; also by Bincer and Hess (28), who obtained improved yields (45 per cent) by a similar method. By treatment of pentaerythritol with the same reagent at 190°C.,

Tollens and Wigand (146) and Rave and Tollens (126) obtained the triiodide, together with a little tetraiodide. The tetraiodide is, however, best prepared by the action of sodium iodide on the tetrabromide in methyl ethyl ketone solution, as reported by Backer and Schurink (15, 135). The diiodide has also been obtained by Backer and Keuning (14) by the reaction of hydriodic acid with 2,6-dioxaspiro[3.3]heptane (VIII).

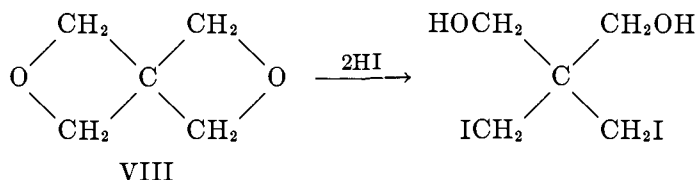
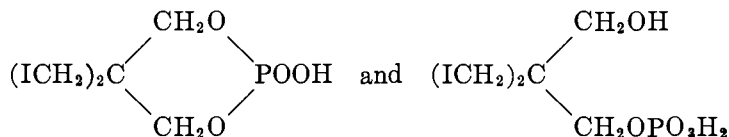


TABLE 2

Pentaerythrityl bromides and derivatives

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
C(CH ₂ Br) ₄	162		(15)
(CH ₂ Br) ₃ CCH ₂ OH.....	66-67		(27)
(CH ₂ Br) ₃ CCH ₂ OCOCH ₃	70-71		(28)
(CH ₂ Br) ₃ C(CH ₂ OH) ₂	44-45		(121)
(CH ₂ Br) ₂ C(CH ₂ OH) ₂	109-110		(28)
(CH ₂ Br) ₂ C(CH ₂ OCOCH ₃) ₂	112		(157)
(CH ₂ Br) ₂ C(CH ₂ OCOC ₆ H ₅) ₂	42		(14)
(CH ₂ Br) ₂ C(CH ₂ OCOC ₆ H ₄) ₂		125/13 mm.	(157)
(CH ₂ Br) ₂ C(CH ₂ OCOC ₆ H ₄ NO _{2-p}) ₂	92		(27)
CH ₂ BrC(CH ₂ OH) ₃	211		(27)
CH ₂ BrC(CH ₂ OCOCH ₃) ₃	76		(68)
	50	159/0.04 mm.	(27)

Eidebenz and Depner (50) have recorded that from the reaction of pentaerythrityl diiodide with phosphorus oxychloride they isolated calcium salts derived from the following acids:



Bincer and Hess (28) have converted the diiodide, by reaction with silver acetate and subsequent acetylation, into pentaerythrityl tetraacetate, and by catalytic hydrogenation in the presence of pyridine and magnesia over palladinized barium sulfate, into 2,2-dimethyltrimethylene glycol.

The melting points of the pentaerythrityl iodides are listed in table 3.

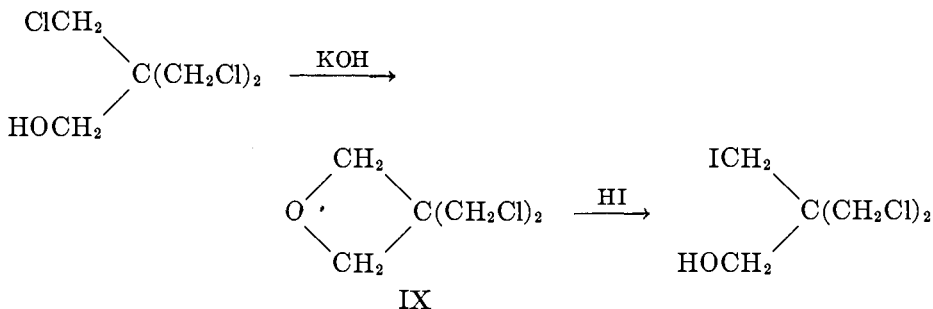
D. Mixed halides

Govaert and Beyaert (72) have prepared mixed trihalogen derivatives indirectly by splitting off hydrogen halide from pentaerythrityl trichloride or tribromide with potassium hydroxide to obtain the corresponding oxacyclobutane derivative (IX), and then opening the ring with another halogen hydride to

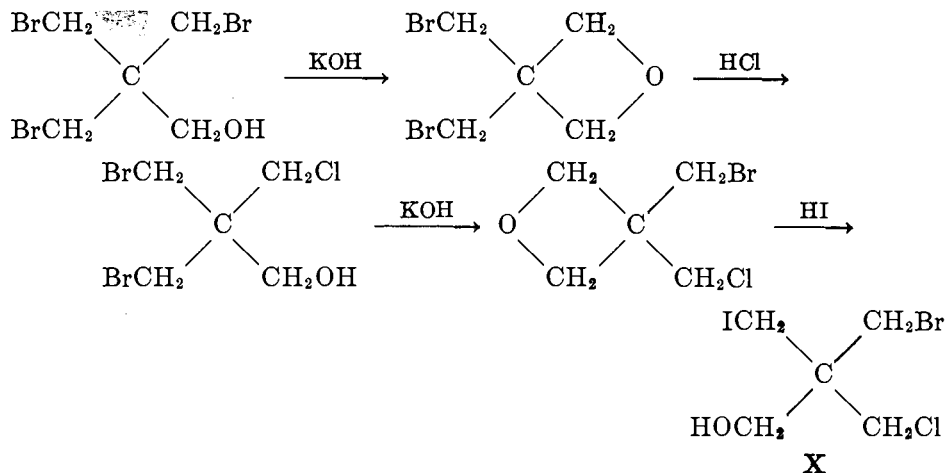
TABLE 3
Pentaerythrityl iodides

COMPOUND	MELTING POINT	REFERENCES
	°C.	
$C(CH_2I)_4$	233	(15, 135)
$(CH_2I)_3CCH_2OH$	62	(146)
$(CH_2I)_2C(CH_2OH)_2$	129.5-130.5	(28)
$CH_2IC(CH_2OH)_3$	106	(68)
$\begin{array}{c} \text{CH}_2\text{O} \\ \diagdown \quad \diagup \\ (\text{CH}_2\text{I})_2\text{C} \quad \text{POOH} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{O} \end{array}$	Isolated as Ca salt	(50)
$\begin{array}{c} \text{CH}_2\text{OH} \\ \diagdown \\ (\text{CH}_2\text{I})_2\text{C} \\ \diagup \\ \text{CH}_2\text{OPO}_3\text{H}_2 \end{array}$	Isolated as Ca salt	(50)

produce the mixed trihalide. The ring closure was reported to give 70-80 per cent yields and the ring opening quantitative yields.



3,3-Bis(iodomethyl)oxacyclobutane was prepared by the action of sodium iodide on an acetone solution of the corresponding dibromide. (Chloromethyl)-(bromomethyl)(iodomethyl)ethanol (X) was prepared by the following series of reactions:



The melting points of the mixed trihalogen derivatives are recorded in table 4.

TABLE 4
Mixed trihalides of pentaerythritol

COMPOUND	MELTING POINT	REFERENCES
	°C.	
HOCH ₂ C(CH ₂ Cl) ₂ (CH ₂ Br).....	55	(72)
HOCH ₂ C(CH ₂ Cl) ₂ (CH ₂ I).....	45	(72)
HOCH ₂ C(CH ₂ Br) ₂ (CH ₂ Cl).....	55	(72)
HOCH ₂ C(CH ₂ Br) ₂ (CH ₂ I).....	54	(72)
HOCH ₂ C(CH ₂ I) ₂ (CH ₂ Cl).....	58	(72)
HOCH ₂ C(CH ₂ I) ₂ (CH ₂ Br).....	55	(72)
HOCH ₂ C(CH ₂ Cl)(CH ₂ Br)(CH ₂ I).....	51	(72)

IV. ESTERS

There are many references in the literature to the resinous esters of pentaerythritol which are prepared from polybasic acids, resin acids, or unsaturated acids. These polymeric materials are omitted from this review.

The tetraesters from pentaerythritol and monobasic acids can be prepared readily from pentaerythritol by the usual methods of reaction with acids, acid chlorides, or acid anhydrides. Barth and Burrell (22) have reported suitable conditions for the preparation of the mono-, di-, and tri-esters from pentaerythritol and the corresponding pentaerythrityl tetraester in the presence of an alkaline catalyst, such as potassium carbonate, at elevated temperatures. Savary (133) has found that esterification of fatty acids with an excess of pentaerythritol in boiling phenol gives mainly monoesters, which can be purified from the other esters by fractional crystallization. Diesters of pentaerythritol have been prepared indirectly by Orthner and Freyss (119) by esterification of the monoisopropylidene derivative, followed by hydrolysis of the ketal grouping.

TABLE 5
 Simple esters of pentaerythritol

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
$C(CH_2OCOH)_4$	57		(130)
$(CH_2OH)_3CCH_2OCOCH_3$			(22)
$(CH_2OH)_2C(CH_2OCOCH_3)_2$	}	207-215/2 mm.	(22)
$CH_2OHC(CH_2OCOCH_3)_3$		159/0.3 mm.	(119)
		176-182/2 mm.	(22)
$C(CH_2OCOCH_3)_4$	84-86		(121, 146)
$C(CH_2OCOCH_2CH_3)_4$	25-30	155-160/2 mm.	(158)
$C[CH_2OCO(CH_2)_2CH_3]_4$		170-175/2 mm.	(84, 158)
$(CH_2OH)_3CCH_2OCO(CH_2)_8CH_3$		185-190/2 mm.	(158)
$(CH_2OH)_3CCH_2OCO(CH_2)_{10}CH_3$	75	Light oil	(159)
$C[CH_2OCO(CH_2)_{10}CH_3]_4$	48.8-49		(39, 102, 133)
$(CH_2OH)_3CCH_2OCO(CH_2)_{12}CH_3$	89		(102, 133)
$C[CH_2OCO(CH_2)_{12}CH_3]_4$	62		(102)
$(CH_2OH)_3CCH_2OCO(CH_2)_{14}CH_3$	96		(102, 133)
$C[CH_2OCO(CH_2)_{14}CH_3]_4$	70-70.5		(1, 2)
$(CH_2OH)_3CCH_2OCO(CH_2)_{16}CH_3$	46-47		(25, 133)
$(CH_2OH)_2C[CH_2OCO(CH_2)_{16}CH_3]_2$	51-52		(25)
$C[CH_2OCO(CH_2)_{16}CH_3]_4$	76.2		(102)
	60-61		(25)
$C[CH_2OCO(CH_2)_7CH=CH(CH_2)_7CH_3]_4$			(29)
$C[CH_2OCOCH=CHCH_2]_4$			(49)
$(CH_2OH)_2C(CH_2OCOC_6H_5)_2$	75		(119)
$C(CH_2OCOC_6H_5)_4$	99-101		(126)
	94		(119)
$(CH_2OH)_3CCH_2OCOC_6H_4NO-o$	105		(144)
$C \left[\begin{array}{c} CH_2OCO \\ \diagdown \quad \diagup \\ \text{C}_6\text{H}_5 \\ \diagup \quad \diagdown \\ CH_2C_6H_5 \end{array} \right]_4$			(57)
$C(CH_2ONO_2)_4$	138-140		(149)
	153-154		(35, 76, 118)
$C(CH_2OSO_3H)_4$			(92)
$C(CH_2OSO_3)_4Ba_2$			(92)
$C(CH_2OSO_3CH_3)_4$	110.5		(92)
$C[CH_2OCOOCH_2C(CH_3)=CH_2]_4$			(111)

The acid tetrasulfate has been prepared from pentaerythritol by Kraft (92) by the action of chlorosulfonic acid, and is easily isolated through its soluble barium salt.

The simple non-polymeric esters which have been prepared from pentaerythritol are listed in table 5.

Van Romburgh (130) has observed that pentaerythrityl tetraformate is split up quantitatively on heating to give carbon monoxide and pentaerythritol. Pentaerythrityl tetraacetate has been found by Baltzly and Buck (20) to be completely hydrolyzed when 0.01 mole of ester in 35–50 cc. of methanol is allowed to stand in contact with 5 cc. of concentrated hydrochloric acid for 24 hr.

With the exception of pentaerythrityl tetranitrate, which is employed for its explosive properties, few of the simple esters have found much commercial application. A few mixed esters have been claimed in the patent literature for use as modifying agents in resins and as explosives, and other esters have been suggested for use in insecticides and as lubricating oil additives (34, 88). Muskat and Strain (111) have prepared pentaerythrityl tetrakis(methyl carbonat) and have found that it polymerizes with benzoyl peroxide at 140°C. The mixed esters can be prepared by further esterification of mono-, di-, and tri-esters;

TABLE 6
Mixed esters of pentaerythritol

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
Diformate dinitrate.....			(152)
Diacetate dinitrate.....			(152)
Diacetate dipropionate.....		173–188/2 mm.	(22)
Diacetate dibutyrate.....		160–165/2 mm.	(22)
Triacetate monopropionate.....		162–164/2 mm.	(22)
Triacetate monostearate.....			(130, 159)
Tripropionate monomyristate.....			(129, 158)
Diglycolic ester, tetranitrate.....		Liquid	(152)
Mono- <i>m</i> -nitrobenzoate trinitrate.....	50–55		(152)
Mono- <i>o</i> -nitrosobenzoate tribenzoate.....	86–88		(144)

a method has also been claimed for the preparation of mixed esters containing the acetyl radical from pentaerythritol in the presence of an organic acid and ketene (123).

The mixed esters of pentaerythritol which have been reported are listed in table 6.

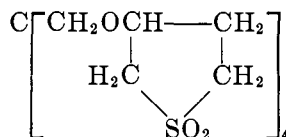
V. ETHERS

The tetraethers from pentaerythritol can be formed readily, and the most convenient method is generally the reaction of pentaerythrityl tetrabromide with the sodium derivative of the alcohol or phenol (5). Ether formation has also been accomplished by the reaction of an alkyl halide with pentaerythritol in presence of alkali (42, 116) and by the reaction of alkyl halide with the sodium derivative of pentaerythritol in liquid ammonia (66). Gustavson and Popper have recorded the preparation of the tetraethyl ether of pentaerythritol by the action of alcoholic potash on pentaerythrityl tetrabromide (80). Pentaery-

thritol has also been reported to react with acrylonitrile (40) and with butadiene sulfone (17) to give tetrakis(2-cyanoethoxymethyl)methane (XI) and tetrakis-(1,1-dioxy-3-thiophanyloxymethyl)methane (XII), respectively.



XI



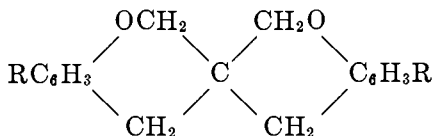
XII

Bruson (41) has found that with crotononitrile, or with allyl cyanide under alkaline conditions (which cause the conversion of the latter to the former), pentaerythritol reacts to give a mixture of bis-, tris-, and tetrakis-(2-cyanoisopropyl) ethers.

The di-*tert*-butyl ether of pentaerythritol has been prepared by the action of *tert*-butyl chloride on pentaerythritol in pyridine solution (5), and the mono-, di-, and tri-methyl ethers of pentaerythritol have been prepared by Orthner and Freyss (119) from monoisopropylidene pentaerythritol.

When pentaerythritol reacts with allyl bromide or methallyl bromide in presence of caustic soda, three ether groupings are introduced. This product can then be converted to the tetraether by reaction with sodium and more of the bromide (115, 116).

Backer and Dijken (5) have examined the action of aluminum chloride on aromatic ethers of pentaerythritol. The tetraphenyl ether gives an isomer for which the structure $\text{C}(\text{CH}_2\text{C}_6\text{H}_4\text{OH})_4$ is suggested, although it does not react with acetyl chloride. This isomer is also formed when pentaerythrityl tetra-bromide reacts with sodium in boiling phenol. The tetra-*p*-chlorophenyl ether and the tetra-*p*-tolyl ether also react in the presence of aluminum chloride to give products to which the structures XIII and XIV are assigned.



XIII: R = Cl

XIV: R = CH₃

The *p*-tolyl ether also produces a small quantity of an isomer, C₃₃H₃₆O₄. Bowman and Barth (36) have reported the action of alkene oxides on pentaerythritol and polypentaerythritols to give ether-alcohol derivatives.

The ethers of pentaerythritol which have been prepared are listed in table 7.

VI. OXACYCLOBUTANE AND 2,6-DIOXASPIRO[3.3]HEPTANE DERIVATIVES

Pentaerythritol, as a polyhydric alcohol, can form intramolecular ether linkages to give a 3,3-disubstituted oxacyclobutane (XV) or 2,6-dioxaspiro[3.3]-heptane (XVI).

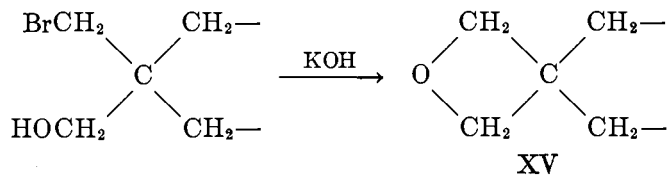
TABLE 7
Ethers from pentaerythritol

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
(CH ₂ OH) ₃ CCH ₂ OCH ₃	72		(119)
Monoisopropylidene derivative.....		129-130/12 mm.	
<i>p</i> -Nitrobenzoate of monoisopropylidene derivative.....	90		
(CH ₂ OH) ₂ C(CH ₂ OCH ₃) ₂	32	139/12 mm.	(119)
(CH ₂ OH) ₂ C(CH ₂ OCH ₃) ₂ dibenzoate.....	70		
CH ₂ OHC(CH ₂ OCH ₃) ₃		103-104/12 mm.	(119)
CH ₂ OHC(CH ₂ OCH ₃) ₃ <i>p</i> -nitrobenzoate...	53-54		
C(CH ₂ OCH ₃) ₄	30-30.5	196-198	(5)
(CH ₂ OH) ₃ CCH ₂ OC ₂ H ₅			(42)
(CH ₂ OH) ₂ C(CH ₂ OC ₂ H ₅) ₂		116/5 mm.	(42, 66)
CH ₂ OHC(CH ₂ OC ₂ H ₅) ₃		94/5 mm.	(42, 66)
C(CH ₂ OC ₂ H ₅) ₄		230-231; 83/5 mm.	(5, 66, 80)
C[CH ₂ O(CH ₂) ₂ CH ₃] ₄		124-127/3 mm.	(5)
CH ₂ OHC(CH ₂ OCH ₂ CH=CH ₂) ₃		114-122/1 mm.	(116)
C(CH ₂ OCH ₂ CH=CH ₂) ₄		124-125/1 mm.	(114, 116)
CH ₂ OHC[CH ₂ OCH ₂ C(CH ₃)=CH ₂] ₃		135-140/0.8 mm.	(115)
C[CH ₂ OCH ₂ C(CH ₃)=CH ₂] ₄		128-129/0.3 mm.	(115)
(CH ₂ OH) ₂ C[CH ₂ OC(CH ₃) ₃] ₂	102-104		(5)
C(CH ₂ OC ₁₆ H ₃₃) ₄	57.5-59		(5)
C(CH ₂ OC ₆ H ₅) ₄	112.5-113.5		(24)
C(CH ₂ OC ₆ H ₄ Cl- <i>p</i>) ₄	141-142		(5)
C(CH ₂ OC ₆ H ₄ Br- <i>p</i>) ₄	153-157		(5)
C(CH ₂ OC ₆ H ₄ CH ₃ - <i>p</i>) ₄	96		(5)
C[CH ₂ OC ₆ H ₄ C(CH ₃) ₃ - <i>p</i>] ₄	168-169		(5)
C[CH ₂ OC ₆ H ₃ Br(<i>o?</i>)C(CH ₃) ₃ - <i>p</i>] ₄	231-232		(5)
C[CH ₂ OC ₆ H ₄ C(CH ₃) ₂ (C ₂ H ₅)- <i>p</i>] ₄	193-194.5		(5)
C(CH ₂ OCH ₂ C ₆ H ₅) ₄		246-250/3 mm.	(5)
C[CH ₂ OC(C ₆ H ₅) ₃] ₄	350		(148)
C $\left[\begin{array}{c} \text{CH}_2\text{OCH} \text{---} \text{CH}_2 \\ \qquad \qquad \\ \text{H}_2\text{C} \qquad \qquad \text{CH}_2 \\ \diagdown \qquad \diagup \\ \text{SO}_2 \end{array} \right]_4$	222.5-223.5		(17)
C(CH ₂ OCH ₂ CH ₂ CN) ₄			(40)
C(CH ₂ OCH ₂ CH ₂ COOC ₄ H ₉) ₄		Not distillable at 1 mm.	(40)
C(CH ₂ OCH ₂ CH ₂ CONH ₂) ₄			(40)
C $\left(\text{CH}_2\text{O} \begin{array}{c} \text{---} \text{C}_6\text{H}_4 \text{---} \\ \\ \text{---} \text{C}_6\text{H}_4 \text{---} \end{array} \right)_4$	170-171.5		(5)

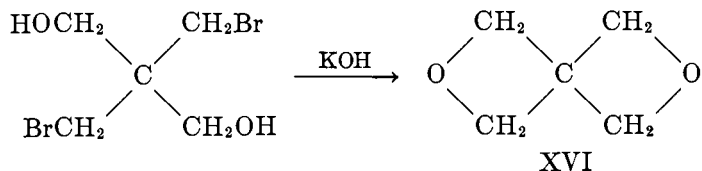
TABLE 7—*Concluded*

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
$\text{C} \left(\begin{array}{c} \text{CH}_2\text{O} \begin{array}{c} \diagup \text{---} \text{---} \diagdown \\ \text{---} \text{---} \end{array} \diagdown \\ \text{---} \text{---} \end{array} \right)_4 \text{ monopicrate} \dots\dots$	200–201.5		
$\text{C} \left(\begin{array}{c} \text{CH}_2\text{O} \begin{array}{c} \diagup \text{---} \text{---} \diagdown \\ \text{---} \text{---} \end{array} \diagdown \\ \text{---} \text{---} \end{array} \right)_4 \dots\dots\dots$	119–120		(5)
$\text{C} \left(\begin{array}{c} \text{CH}_2\text{O} \begin{array}{c} \diagup \text{---} \text{---} \diagdown \\ \text{---} \text{---} \end{array} \diagdown \\ \text{---} \text{---} \end{array} \right)_4 \text{ dipicrate} \dots\dots\dots$	189.5–190.5		
$\text{CH}_3\text{OCH}_2\text{C}(\text{CH}_2\text{ONO}_2)_3 \dots\dots\dots$	79–80		(131, 152)
$(\text{CH}_3\text{OCH}_2)_2\text{C}(\text{CH}_2\text{ONO}_2)_2 \dots\dots\dots$	53–54		(152)
$\text{C}_2\text{H}_5\text{OCH}_2\text{C}(\text{CH}_2\text{ONO}_2)_3 \dots\dots\dots$			(132)

The general method for the preparation of oxacyclobutane derivatives is by the action of potassium hydroxide on a pentaerythrityl halide (26, 59, 70, 71, 72).



Attempts made to prepare 2,6-dioxaspiro[3.3]heptane by the action of sodium on pentaerythrityl dibromide, potassium hydroxide on pentaerythrityl dibromide diacetate, sulfuric acid on pentaerythritol, and potassium hydroxide on pentaerythrityl dichloride were all without success. Backer and Keuning (14) obtained the required material by the action of alcoholic potash on pentaerythrityl dibromide.



2,6-Dioxaspiro[3.3]heptane is a solid which is volatile at ordinary temperatures. The ether linkages are split readily with hydriodic acid to give 2,2-bis(iodomethyl)-1,3-propanediol.

Oxacyclobutane and dioxaspiroheptane derivatives prepared from pentaerythritol are listed in table 8.

TABLE 8

Oxacyclobutane and 2,6-dioxaspiro[3.3]heptane derivatives prepared from pentaerythritol

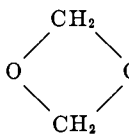
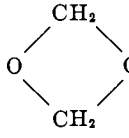
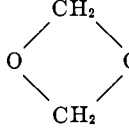
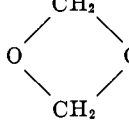
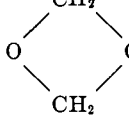
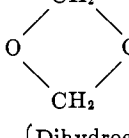
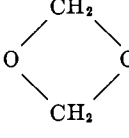
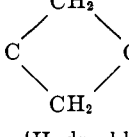
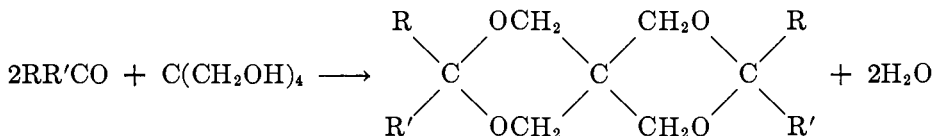
COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
	84	128/0.04 mm.	(71)
	19		(72)
	25	121/1.8 mm.	(26, 72)
	49		(72)
	16		(72)
		122/1.5 mm.	(26)
{ Dihydrochloride.....	234		(26)
{ Dipicrate.....	237 d.		(26)
{ Dioxalate.....	154 d.		(26)
	79		(26, 70)
		132/14 mm.	(59)
{ Hydrochloride.....	135.5		(59)

TABLE 8—*Concluded*

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
	142		(59)
	89	172	(14)
	130-132		(14)

VII. ACETALS AND KETALS

Pentaerythritol readily forms acetals and ketals, and these have been the subject of a fair volume of work on account of their spirocyclic nature.



Tollens (4, 134), Read (127), and Radulescu (124) used hydrochloric and sulfuric acids as condensing agents with a variety of aldehydes. Böeseken and Felix (31) have used alcoholic hydrogen chloride for the preparation of ketals from carboxylic ketones, and Backer and Schurink (16) have employed zinc chloride. Mkhitarian (107) found that pentaerythritol diacetals can be prepared in good yield, uncontaminated by the monoacetals, by the reaction of pentaerythritol with acetals in the presence of a small quantity of *p*-toluene-sulfonic acid. Orthner (118) has used anhydrous copper sulfate as a condensing agent.

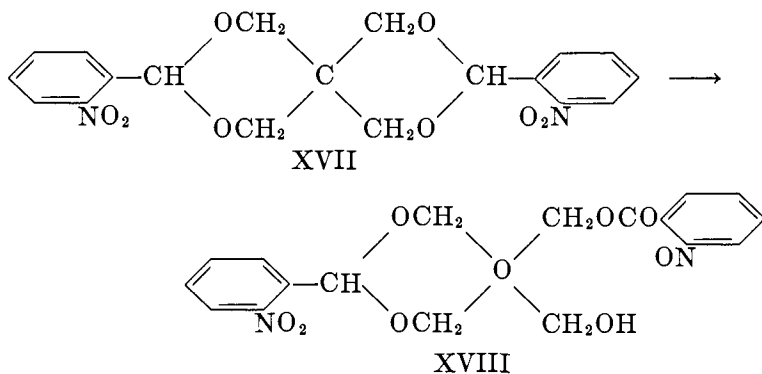
The preparation of monoacetals and monoketals from pentaerythritol has been reported by Böeseken (30, 31, 32, 33), Skrabal (140, 141), Orthner (118, 119), Tanasescu (143, 144), Fairbourne and Woodley (53), and British Celanese Ltd. (38). Their separation from the corresponding diacetals and diketals can generally be accomplished by solubility differences. Fairbourne and Woodley found that when 50 per cent sulfuric acid was used as the condensing agent for *p*-dimethylaminobenzaldehyde and pentaerythritol the proportion of monoacetal was much higher than when 10 per cent sulfuric acid was used. These authors,

and also Tanasescu and Ilescu (144), have found that on attempting to prepare a mixed acetal from a monoacetal, by reaction with another aldehyde, the original alkylidene radical was eliminated with formation of the diacetal derived from the second aldehyde.

Nieuwland, Vogt, and Foohey (113) have prepared diethylidenepentaerythritol from pentaerythritol and acetylene in the presence of a boron trifluoride-alcohol-mercury catalyst.

Böeseken and Felix (31) have reported that in a preparation of the dibenzylidene acetal of pentaerythritol from benzylidene acetal and pentaerythritol, they obtained an optically active product by spontaneous resolution of the racemate. They were unable to repeat the preparation, but have resolved other acetals and ketals by the usual methods (32, 33).

Tanasescu (143, 144, 145) has investigated the action of sunlight on the di-*o*-nitrobenzylidene acetal of pentaerythritol (XVII). The material developed a yellow color, and only one of the acetal groupings was affected, the product being the mono-*o*-nitrosobenzoate of mono-*o*-nitrobenzylidenepentaerythritol (XVIII).



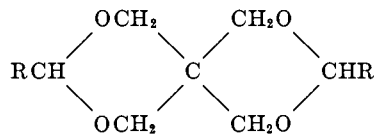
The crude reaction product was separated into two isomers, both of which gave the same benzoate; on hydrolysis both gave the same *o*-nitrobenzylidenepentaerythritol. One isomer was converted to the other on careful heating and it is suggested that they are *cis* and *trans* isomers. Mono-*o*-nitrobenzylidenepentaerythritol also undergoes reaction in sunlight, being converted to pentaerythritol mono-*o*-nitrosobenzoate.

Contardi and Ciocca (44) have recorded that formaldehyde, at ordinary temperature, reacts with pentaerythritol to give an equilibrium mixture containing the hemiacetal.

A method for the estimation of pentaerythritol as its dibenzylidene derivative has been reported by Kraft (91).

It has been claimed by Scott (136) that the dimethylene ether of pentaerythritol is a suitable medium for the reaction of sodium with certain hydrocarbons (e.g., naphthalene). When the sodium derivatives formed are treated with carbon dioxide, carboxylic acids result.

TABLE 9
Acetals from pentaerythritol



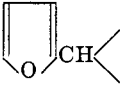
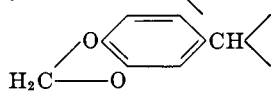
RCH<	MELTING POINT	BOILING POINT	REFERENCES	
	°C.	°C.		
CH ₂ <.....	50		(127, 134, 141)	
CH ₃ CH<.....	40; 45	113/14 mm.	(113)	
CH ₃ CH ₂ CH<.....			(140, 141)	
CH ₃ CH ₂ CH<.....	25	250-252	(140, 141)	
CH ₂ (CH ₂) ₂ CH<.....	60-65		(107)	
(CH ₃) ₂ CHCH<.....	95		(140, 141)	
$ \begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CHCH} < \\ \diagup \\ \text{C}_2\text{H}_5 \end{array} $	110-112		(107)	
CH ₃ (CH ₂) ₃ CH<.....	63		(127)	
CH ₂ ClCH<.....	91.8		(107)	
CH ₂ (NH ₂)CH<.....	$ \left\{ \begin{array}{l} dl..... \\ l..... \\ d..... \end{array} \right. $		(33)	
				62-64
				60-70
CCl ₂ CH<.....	72-74			
CCl ₂ CH<.....	275		(31)	
CBr ₂ CH<.....	248-249		(16)	
	161		(127)	
	164.5-165		(16)	
C ₆ H ₅ CH<.....	160		(4, 31, 124, 127)	
	188-189			
<i>o</i> -O ₂ NC ₆ H ₄ CH<.....	163-164		(124, 127, 143)	
	166		(144, 145)	
<i>m</i> -O ₂ NC ₆ H ₄ CH<.....	185		(127)	
	188-189		(124)	
<i>p</i> -O ₂ NC ₆ H ₄ CH<.....	229		(127)	
	236-237		(124)	

TABLE 9—*Concluded*

RCH<	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
<i>o</i> -H ₂ NC ₆ H ₄ CH< (amorphous).....	164		(124)
<i>o</i> -H ₂ NC ₆ H ₄ CH< hydrochloride.....	172		(124)
<i>m</i> -H ₂ NC ₆ H ₄ CH<.....	225		(124)
<i>m</i> -(CH ₃) ₂ NC ₆ H ₄ CH<.....			(31)
<i>p</i> -(CH ₃) ₂ NC ₆ H ₄ CH<.....	223		(124)
<i>p</i> -(CH ₃) ₂ NC ₆ H ₄ CH< monomethiodide.....	220 d.		(53)
<i>m</i> -HO ₃ SC ₆ H ₄ CH<.....			(31)
<i>m</i> -HOCC ₆ H ₄ CH<.....			(31)
C ₆ H ₅ CH=CHCH<.....	195		(127)
<i>p</i> -CH ₃ OC ₆ H ₄ CH<.....	177		(127)
	188		(127)

Diacetals and diketals from pentaerythritol are listed in tables 9 and 10 and monoacetals and ketals in table 11.

VIII. AMINES

Govaert (67) first reported the preparation of the tetramine derived from pentaerythritol, C(CH₂NH₂)₄. Pentaerythrityl tetrabromide on reaction with liquid ammonia gave small quantities of the amine, and when heated in a sealed vessel at 180–190°C. with a saturated solution of ammonia in ethanol, a 35 per cent yield was obtained. The hydrochloride was reported to lose ammonium chloride in hot aqueous solution to give the dihydrochloride of 2,6-diazaspiro-[3.3]heptane (XIX).

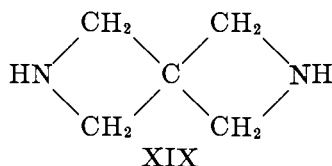
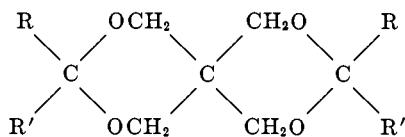


TABLE 10
Ketals from pentaerythritol



$ \begin{array}{c} R \\ \diagdown \\ C \\ \diagup \\ R' \end{array} $	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
$ \begin{array}{c} CH_3 \\ \diagdown \\ C \\ \diagup \\ CH_3 \end{array} \dots\dots\dots $	116		(30, 118, 140, 141)
$ \begin{array}{c} CH_2CH_2 \\ \diagdown \\ C \\ \diagup \\ CH_2CH_2 \end{array} \dots\dots\dots $	153-155		(16)
$ \begin{array}{c} CH_2CH_2 \\ \diagdown \\ C \\ \diagup \\ CH_2CH_2 \end{array} \dots\dots\dots $	115.5		(16)
$ \begin{array}{c} CH_2-CH_2 \\ \diagdown \\ C \\ \diagup \\ CH-CH_2 \\ \\ CH_3 \end{array} \dots\dots\dots d $	79-81		(30)
$ \begin{array}{c} CH_3 \\ \diagdown \\ C \\ \diagup \\ C_2H_5OOC \end{array} \dots\dots\dots $	46	145 130-135*	(31) (32)
$ \begin{array}{c} CH_3 \\ \diagdown \\ C \\ \diagup \\ HOOC \end{array} \dots\dots\dots $	235		(31) (32)

TABLE 10—*Concluded*

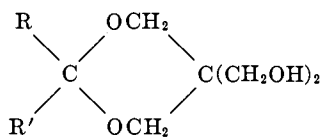
$\begin{array}{c} R \\ \diagdown \\ C \\ \diagup \\ R' \end{array}$	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
$\begin{array}{c} CH_3 \\ \diagdown \\ C \\ \diagup \\ C_2H_5OOCCH_2 \end{array}$		145-150*	(31)
$\begin{array}{c} CH_3 \\ \diagdown \\ C \\ \diagup \\ HOOCCH_2 \end{array}$	Loses CO ₂ at 100°C.		(31)
$\begin{array}{c} CH_3 \\ \diagdown \\ C \\ \diagup \\ HOOCCH_2CH_2 \end{array}$	186-188		(31)
$\begin{array}{c} CH_2CH_2 \\ \diagup \\ C_2H_5OOCCH \\ \diagdown \\ CH_2CH_2 \\ \diagup \\ C \\ \diagdown \end{array}$	139.5-140.5		(122)
$\begin{array}{c} CH_2-CH-CH_2 \\ \\ C(CH_3)_2 \\ \\ CH_2-C(CH_3)-C \\ \diagdown \end{array}$	156		(33)

* High vacuum.

Contrary to this finding, Litherland and Mann (96) recorded that the tetrahydrochloride of the tetramine possessed great stability and was recovered unchanged from boiling in water for 36 hr., boiling in hydrochloric acid for 20 hr., and from treatment with hydrochloric acid at 160°C. for 5 hr.

Van Alphen (3) investigated the action of ammonia on pentaerythrityl tetrabromide and found that a mixture of highly condensed amines resulted, with only a little of the tetramine. Litherland and Mann (96, 100) have prepared the tetramine from pentaerythrityl tetrabromide by a two-stage process, which they claim as being convenient for the preparation of large quantities. The tetrabromide was heated with sodium *p*-toluenesulfonamide for 10 hr. at 210°C. to give tetrakis(*p*-toluenesulfonamidomethyl)methane (XX) as the chief product. On hydrolysis of this with 80 per cent sulfuric acid, the disulfate of the tetramine

TABLE 11
Monoacetals and ketals from pentaerythritol



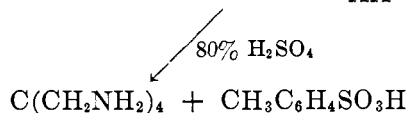
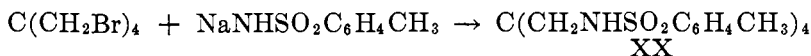
$ \begin{array}{c} \text{R} \\ \diagdown \\ \text{C} \\ / \\ \text{R}' \end{array} $	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
CH ₂ <	60		(140)
CH ₂ < diacetate		298	(38)
CH ₂ < dipropionate		312	(38)
CH ₂ < dibutyrate		336	(38)
CH ₂ < dibenzoate	94-96		(38)
CH ₃ CH<	104		(140)
CH ₃ CH< diacetate		310	(38)
NH ₂ CH ₂ CH<	124		(33)
CH ₃ CH ₂ CH<	70		(140)
CH ₃ CH ₂ CH ₂ CH< diacetate		345	(38)
(CH ₃) ₂ CHCH<	107		(140)
(CH ₃) ₂ C<	135		(30, 140, 141, 118)
{ Diacetate	48-49		(119)
{ Dibenzoate	110		(119)
$ \begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} \\ / \\ \text{C}_2\text{H}_5\text{OOC} \end{array} $	95	145-165*	(31) (32)
<i>o</i> -O ₂ NC ₆ H ₄ CH<	145		(143)
{ Mono- <i>o</i> -nitrosobenzoate	85 and 135		(143)
(<i>cis</i> and <i>trans</i> isomers)			
{ Mono- <i>o</i> -nitrosobenzoate monobenzoate	83-84		(143)
{ Dibenzoate	109-110		(144)
{ Mono- <i>o</i> -azobenzoate	110		(144)

* High vacuum.

TABLE 11—Concluded

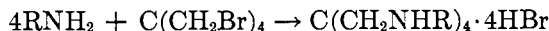
$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{R}' \end{array}$	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
$p\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{CH} \left\{ \begin{array}{l} \dots\dots\dots \\ \dots\dots\dots \end{array} \right.$	140 d.		(53)
$p\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{CH} \left\{ \begin{array}{l} \dots\dots\dots \cdot \text{CH}_3\text{I} \dots\dots\dots \\ \dots\dots\dots \end{array} \right.$	175 d.		(53)
$\begin{array}{c} \text{CH}_2\text{---CH---CH}_2 \\ \quad \quad \\ \quad \quad \\ \text{C(CH}_3)_2 \\ \quad \quad \\ \text{CH}_2\text{---C(CH}_3\text{)---C} \left\{ \begin{array}{l} \dots\dots\dots \\ \dots\dots\dots \end{array} \right. \end{array}$	135		(33)

was obtained and readily gave the free base, which was isolated as the tetrahydrate (63).

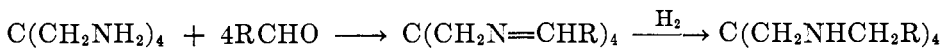


Govaert and Beyaert (69) isolated the tetramine as the monohydrate.

N-Tetrasubstituted pentaerythrityltetramine derivatives can be prepared readily, and generally in good yield, by reaction of the tetrabromide with the corresponding amine (3).



Secondary amines have also been prepared from pentaerythrityltetramine by condensation with aldehydes, followed by reduction of the products (3).

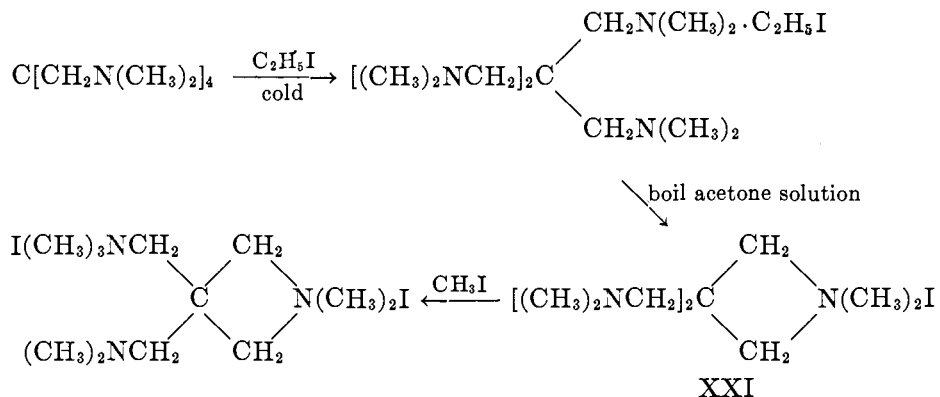


Litherland and Mann (96) found that methylation of pentaerythrityltetramine gave the octamethyl derivative, tetrakis(dimethylaminomethyl)methane, $\text{C}[\text{CH}_2\text{N(CH}_3)_2]_4$, and that although this gave a tetrapicrate and tetrahydrochloride, it could not be induced to combine directly with 4 molecules of methyl iodide, giving instead the biquaternary iodide $\text{C}[\text{CH}_2\text{N(CH}_3)_2]_2[\text{CH}_2\text{N(CH}_3)_3\text{I}]_2$. When this biquaternary iodide was heated above its melting point, effervescence occurred and the quadriquaternary salt, $\text{C}[\text{CH}_2\text{N(CH}_3)_3\text{I}]_4$, was isolated.

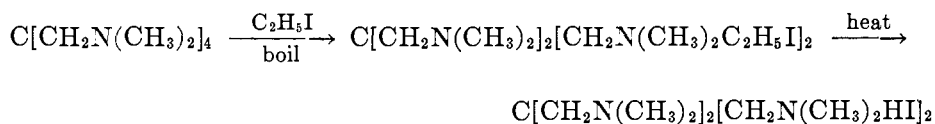
Govaert and Cazier (74) have prepared the quadriquaternary bromide $\text{C}[\text{CH}_2\text{N(CH}_3)_3\text{Br}]_4$ by the reaction of pentaerythrityl tetrabromide with trimethylamine in alcoholic solution at 230°C. for 18 hr. The same authors (75) have also reported the isolation of this compound from the product of reaction

of pentaerythryl dibromide with trimethylamine in alcoholic solution at 150°C. for 20 hr.

Gibson and Mann (64) have also studied other quaternary salts of the octamethyl base. On treatment of tetrakis(dimethylaminomethyl)methane with ethyl iodide in the cold, a monoethiodide was obtained and when this was boiled in acetone solution it was converted to 3,3-bis(dimethylaminomethyl)-*N*-methyltrimethyleneimine monomethiodide (XXI), which with an excess of methyl iodide combined with only one more molecule.



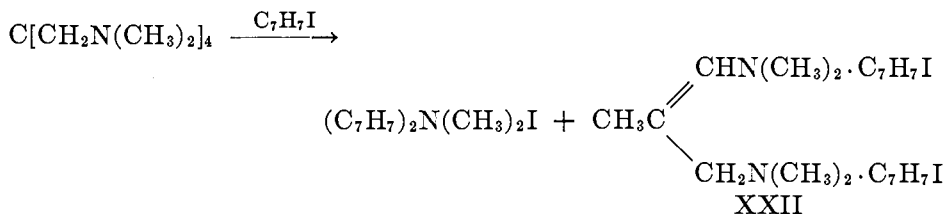
When, however, the octamethyl base was boiled with ethyl iodide, a diethiodide resulted; on heating, this was converted to the dihydriodide of the original octamethyl base with elimination of a gas, probably ethylene.



Reaction of the octamethyl base with an excess of allyl iodide in the cold produced the monoallyliodide, which, when heated, also produced 3,3-bis(dimethylaminomethyl)-*N*-methyltrimethyleneimine monomethiodide (XXI). When the monoallyliodide was treated with an excess of methyl iodide, it gave the monoallyliodide monomethiodide.

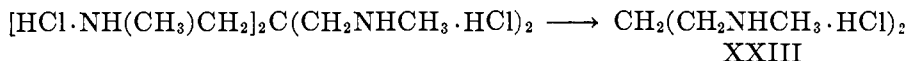
From the reaction of the octamethyl base with an excess of allyl iodide in the cold there was also produced the monoallyliodide monohydriodide, which on fusion gave the dihydriodide of the octamethyl base, a reaction similar to that of the diethiodide.

The reaction of benzyl iodide with tetrakis(dimethylaminomethyl)methane followed those with ethyl and allyl iodides, but with certain differences. When the octamethyl base and benzyl iodide were mixed without solvent, there were obtained dibenzyl dimethylammonium iodide and the dibenzyl iodide of 1,3-bis(dimethylamino)-2-methylpropene (XXII).



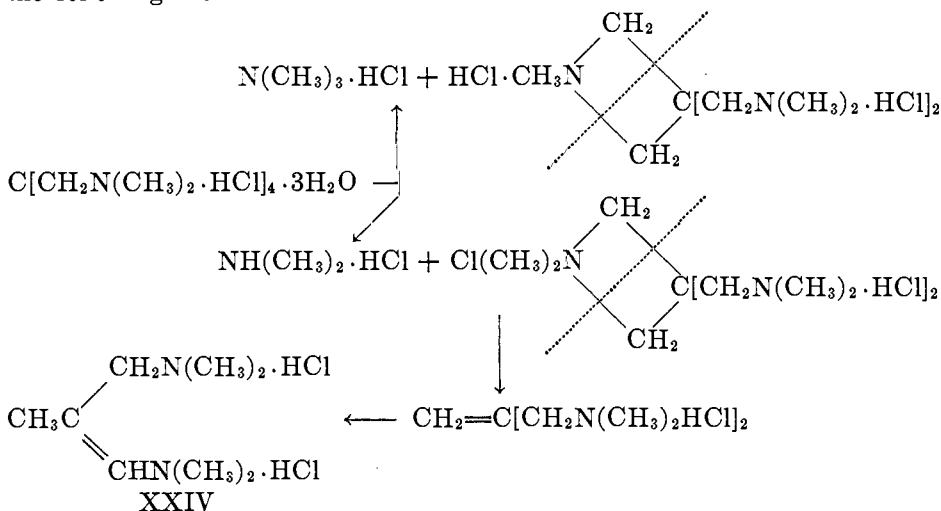
When benzyl iodide was mixed with the octamethyl base in ether solution, there was obtained the monobenzyl iodide of the base, the dibenzyl iodide of the base, and the monobenzyl iodide monohydriodide of the base. The monobenzyl iodide behaved similarly to the monoethiodide and the monoallyliodide on heating, giving the trimethyleneimine derivative (XXI), and the dibenzyl iodide behaved similarly to the diethiodide on heating in giving the dihydriodide of the octamethyl base.

Gibson, Harley-Mason, Litherland, and Mann (63) have reported the transformations undergone by the hydrochlorides of tetrakis(methylaminomethyl)methane, $\text{C}(\text{CH}_2\text{NHCH}_3)_4$, and tetrakis(dimethylaminomethyl)methane, $\text{C}[\text{CH}_2\text{N}(\text{CH}_3)_2]_4$, on heating. The tetrahydrochloride of the tetramethyl base when heated to just above its melting point decomposes to give the dihydrochloride of 1,3-bis(methylamino)propane (XXIII).

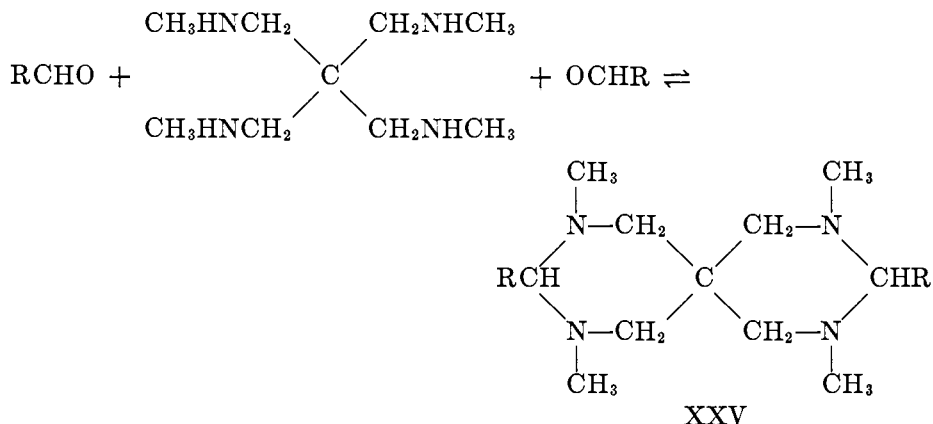


This is a reaction of the salt only, the free base being volatile without decomposition.

When the hydrated hydrochloride of the octamethyl base is heated above its melting point, formaldehyde is evolved and the residue contains the hydrochlorides of mono-, di-, and tri-methylamines, together with the hydrochloride of 1,3-bis(dimethylamino)-2-methylpropene (XXIV). The authors suggest the following mechanism:



Tetrakis(methylaminomethyl)methane condenses readily with aldehydes to give derivatives of 2,4,8,10-tetramethyl-2,4,8,10-tetraazaspiro[5.5]undecane (XXV), which are readily hydrolyzed back to the amine and the aldehyde by dilute acids.



Derivatives of tetrakis(aminomethyl)methane are listed in table 12 and those of 2,4,8,10-tetramethyl-2,4,8,10-tetraazaspiro[5.5]undecane in table 13.

Beyaert and Govaert (26) have prepared the triamino derivative of pentaerythritol indirectly from pentaerythryl tribromide. Reaction of the bromide with the theoretical amount of potassium hydroxide produced 3,3-bis(bromomethyl)oxacyclobutane (XXVI) in 79 per cent yield and from this the corresponding 3,3-bis(aminomethyl)oxacyclobutane (XXVII) was obtained by the action of liquid, alcoholic, or aqueous ammonia at room temperature. The oxacyclobutane ring was opened by aqueous ammonia at 200°C. to give the triamino compound (XXVIII). The substitution of NH₂ for Br, and the ring opening with ammonia were also carried out in one step by reaction of the bis-(bromomethyl)oxacyclobutane with ammonia at 200°C.

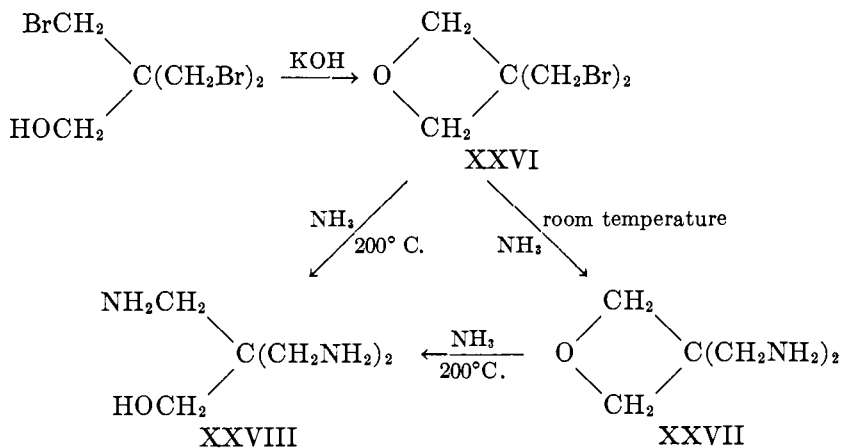


TABLE 12
Derivatives of tetrakis(aminomethyl)methane

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
$C(CH_2NH_2)_4 \cdot H_2O$	41-42	278-282 108/0.7 mm.	(3, 69)
$C(CH_2NH_2)_4 \cdot 4H_2O$	100-100.5		(63)
$C(CH_2NH_2)_4 \cdot 4HCl$	Decomposes above ca. 260		(96)
$C(CH_2NH_2)_4 \cdot 4HBr$			(67, 69)
$C(CH_2NH_2)_4 \cdot HNO_3$	220-222		(67)
$C(CH_2NH_2)_4 \cdot (H_2SO_4)_2$	303		(96)
$C(CH_2NH_2)_4$ tetrapicrate.....	196-197		(96)
	206-208		(3)
$C(CH_2NH_2)_4 \cdot 2H_2CO_3$	125 with loss of CO_2		(69)
$C(CH_2NH_2)_4 \cdot 2HgCl_2$			(69)
$C(CH_2NHCOCH_3)_4$	60	72.5-73/2 mm.	(69)
$C(CH_2NHCOC_6H_5)_4$	276		(96)
$C(CH_2NH SO_2 C_6H_4 CH_3-p)_4$	248		(96)
$C(CH_2NH SO_2 C_6H_4 NH_2-p)_4$	243.5-244		(96)
$C(CH_2NH SO_2 C_6H_4 NHCOCH_3-p)_4$	304-306		(96)
$C(CH_2NHCONH_2)_4$	230 d.		(69)
$C(CH_2NHNH_2)_4 \cdot 5HBr \cdot 3H_2O$	Decomposes at 207		(3)
$C(CH_2NHCSNHC_6H_5)_4$	Decomposes at 150		(3)
$C(CH_2N=CHC_6H_5)_4$	330		(3)
$C(CH_2N=CHC_6H_4Cl-p)_4$	272		(3)
$C(CH_2N=CHC_6H_4NO_2-p)_4$	178		(3)
$C\left(CH_2N=CH \begin{array}{c} \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array} CH_2\right)_4$	130		(3)
$C(CH_2NHCH_3)_4 \cdot 2H_2O$		235-238 245-248	(3) (63)
$C(CH_2NHCH_3)_4 \cdot 4HCl$	264 d.		(63)
$C(CH_2NHCH_3)_4 \cdot 4HBr$	266 d.		(63)
$C(CH_2NHCH_3)_4$ tetrapicrate.....	190-195		(3)
$C[CH_2N(CH_3)CSNHC_6H_5]_4$	152 d.		(3)
$C[CH_2N(CH_3)SO_2C_6H_5]_4$	239		(63)
$C(CH_2NHCH_2CH_2NH_2)_4$		265-275	(3)
$C(CH_2NCH_2CH_2NHCSNHC_6H_5)_4$	130-135		(3)
 CSNHC ₆ H ₅			
$C(CH_2NHCH_2CH_2NHCH_2C_6H_5)_4$ hydro- chloride.....	140-160 d.		(3)

TABLE 12—*Concluded*

COMPOUND	MELTING POINT	BOILING POINT	REFERENCES
	°C.	°C.	
$C(CH_2NHCH_2C_6H_5)_4$ hydrochloride.....	217-218		(3)
$C[CH_2N(CH_3)_2]_4$		248-249/769 mm. 157/45 mm.	(63)
$C[CH_2N(CH_3)_2]_4 \cdot 4HCl$	231		(96)
$C[CH_2N(CH_3)_2]_4 \cdot 2HI$	208-209		(64)
$C[CH_2N(CH_3)_2]_4 \cdot 2CH_3I$	149 d.		(96)
$C[CH_2N(CH_3)_2]_4 \cdot 4CH_3I$	Sublimes above 350		(96)
$C[CH_2N(CH_3)_2]_4 \cdot 4CH_3Cl$	Sublimes above 330		(74)
$C[CH_2N(CH_3)_2]_4 \cdot 4CH_3ClO_4$	Decomposes ex- plosively at 380		(74)
$C[CH_2N(CH_3)_2]_4$ tetramethopicrate.....	310 d.		(74)
$C[CH_2N(CH_3)_2]_4 \cdot 2C_2H_5I$	128		(64)
$C[CH_2N(CH_3)_2]_4 \cdot C_3H_5I$	145-146		(64)
$C[CH_2N(CH_3)_2]_4 \cdot C_3H_5I \cdot HI$	157-158		(64)
$C[CH_2N(CH_3)_2]_4 \cdot C_3H_5I \cdot CH_3I$	114-115 d.		(64)
$C[CH_2N(CH_3)_2]_4 \cdot C_6H_5CH_2I$	146-147		(64)
$C[CH_2N(CH_3)_2]_4 \cdot 2C_6H_5CH_2I$	128-129 d.		(64)
$C[CH_2N(CH_3)_2]_4 \cdot C_6H_5CH_2I \cdot HI$	170		(64)
$C[CH_2N(CH_3)_2]_4 \cdot C_3H_5I \cdot C_6H_5CH_2I$	145-146 d.		(64)
$C \left(\begin{array}{c} CH_2CH_2 \\ \diagdown \quad \diagup \\ CH_2N \quad CH_2 \\ \diagup \quad \diagdown \\ CH_2CH_2 \end{array} \right)_4$	163		(3)
$C \left(\begin{array}{c} CH_2CH_2 \\ \diagdown \quad \diagup \\ CH_2N \quad NH \\ \diagup \quad \diagdown \\ CH_2CH_2 \end{array} \right)_4$			(3)
$C \left(\begin{array}{c} H_2C \quad \quad CH_2 \\ \quad \quad \\ CH_2N \quad CH_2 \\ \diagdown \quad \diagup \\ CS \end{array} \right)_4$	Decomposes above 320		(3)
$C[CH_2N(NO_2)C_6H_4(NO_2)_{3-o,p}]_4$	117		(3)

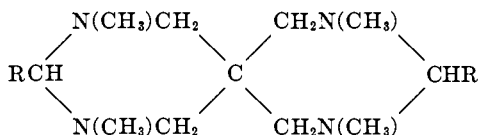
Fourneau, Matti, and Dunant (59) have prepared derivatives of the triamine by reaction of pentaerythryl tribromide with primary and secondary amines at 130-140°C.

In the preparation of tetrakis(*p*-toluenesulfonamidomethyl)methane (XIX) from pentaerythrityl tetrabromide and sodium *p*-toluenesulfonamide, Litherland and Mann (96) found that there was always obtained, as a by-product, a small quantity of *N*-*p*-toluenesulfonyl-3,3-bis(*p*-toluenesulfonamidomethyl)trimethyleneimine (XXIX). Hydrolysis of the toluenesulfonyl groups and ring opening were accomplished by heating with 70 per cent sulfuric acid, giving hydroxymethyltris(aminomethyl)methane (XXVIII). This triamine gave a tetrabenzoyl derivative, but even with an excess of *o*-nitrobenzoyl chloride only the tri-*o*-nitrobenzoyl derivative could be isolated.

When the trisulfonamide derivative (XXIX) was heated with concentrated hydrochloric acid, ring opening occurred and chloromethyltris(*p*-toluenesul-

TABLE 13

2,4,8,10-Tetramethyl-2,4,8,10-tetraazaspiro[5.5]undecane derivatives

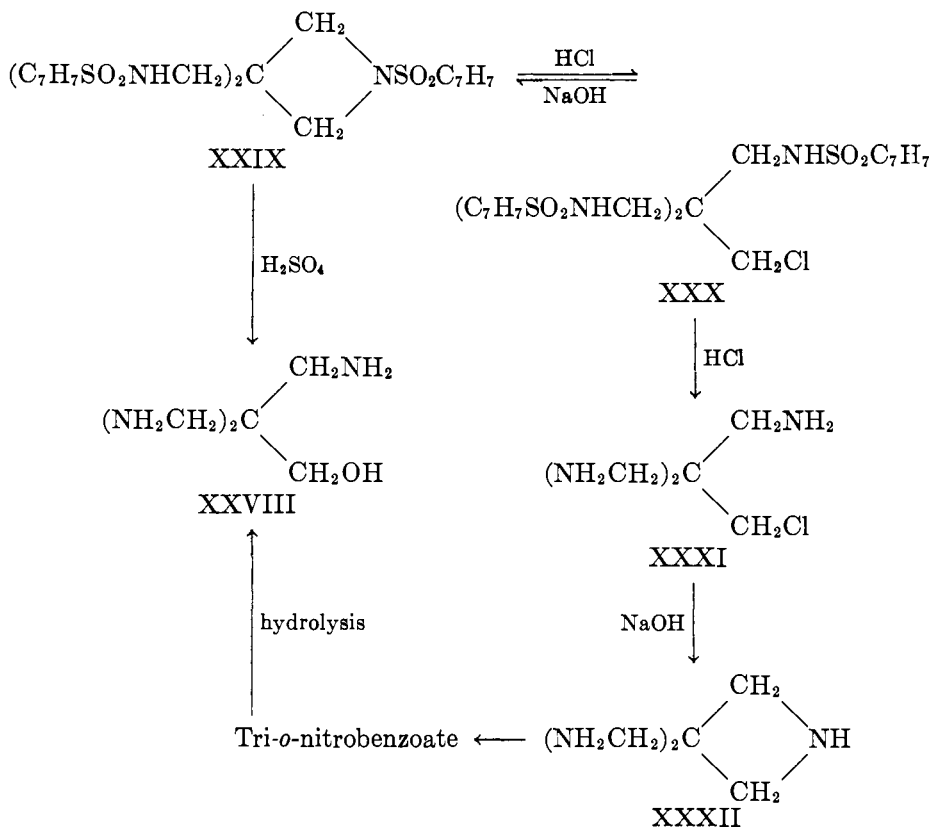


COMPOUND	MELTING POINT	REFERENCE
	°C.	
R = C ₆ H ₅	110	(3)
= C ₆ H ₄ NO ₂ - <i>p</i>	230	(3)
= C ₆ H ₄ Cl- <i>p</i>	220	(3)
= C ₆ H ₄ OCH ₃ - <i>p</i>	164	(3)
= C ₆ H ₃ (O ₂ CH ₂) (3,4-).....	153	(3)
$ \begin{array}{c} \text{N(CH}_3\text{)CH}_2 \quad \quad \quad \text{CH}_2\text{N(CH}_3\text{)} \\ \diagdown \quad \quad \quad \diagup \quad \quad \quad \diagdown \\ \text{SC} \quad \quad \quad \text{C} \quad \quad \quad \text{CS} \dots\dots\dots \\ \diagup \quad \quad \quad \diagdown \quad \quad \quad \diagup \\ \text{N(CH}_3\text{)CH}_2 \quad \quad \quad \text{CH}_2\text{N(CH}_3\text{)} \end{array} $	Decomposes at about 260	(3)

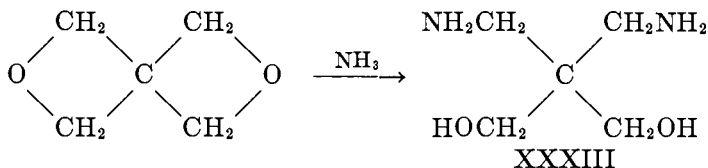
fonamidomethyl)methane (XXX) was formed. This reaction was reversed by caustic soda. Further hydrolysis with hydrochloric acid removed the toluenesulfonyl residues to give chloromethyltris(aminomethyl)methane (XXXI), and steam distillation of this chlorotriamine in alkaline solution converted it to 3,3-bis(aminomethyl)trimethyleneimine (XXXII). On hydrolysis of the tri-*o*-nitrobenzoyl derivative of this compound, ring fission occurred to give the monohydroxytriamine (XXVIII).

The derivatives of hydroxymethyltris(aminomethyl)methane are listed in table 14 and 3,3-disubstituted trimethyleneimine derivatives prepared from pentaerythritol are listed in table 17.

Govaert and Beyaert (70) have prepared 2,2-bis(aminomethyl)-1,3-propane-



diol (XXXIII) in 78 per cent yield by the action of aqueous ammonia on 2,6-dioxaspiro[3.3]heptane at 190°C. for 12 hr.



In an attempt to prepare this diamine from pentaerythrityl dibromide and alcoholic ammonia, they report that only 3,3-bis(acetaminomethyl)oxacyclobutane was isolated in low yield after acetylation of the reaction product. Reaction was also attempted with liquid ammonia at 100°C. and was found to occur readily, but no definite product could be separated from the reaction mixture.

Fourneau, Matti, and Dunant (59) have reported the preparation of alkyl derivatives of the diamine by reaction of pentaerythrityl dibromide with primary or secondary amines at 130–140°C.

Govaert and Cazier (75) have prepared 2,2-bis(dimethylaminomethyl)-1,3-propanediol by reacting 2,6-dioxaspiro[3.3]heptane with aqueous dimethylamine at 215°C. Derivatives of 2,2-bis(aminomethyl)-1,3-propanediol are listed in table 15.

Govaert and Beyaert (71) have also reported the preparation of the monoamine derived from pentaerythritol,—aminomethyltris(hydroxymethyl)methane. They carried out their reaction from pentaerythrityl monobromide in two stages. Reaction of the bromide with potassium hydroxide gave an 81 per cent yield of 3,3-bis(hydroxymethyl)oxacyclobutane (XXXIV) and the ring opening was

TABLE 14
Derivatives of hydroxymethyltris(aminomethyl)methane

COMPOUND	MELTING POINT	BOILING POINT	REFER- ENCE
	°C.	°C.	
CH ₂ OHC(CH ₂ NH ₂) ₃	121	131/0.11 mm.	(26)
CH ₂ OHC(CH ₂ NH ₂) ₃ ·3HCl.....	298 d.		(96)
CH ₂ OHC(CH ₂ NH ₂) ₃ ·3HNO ₃	239 d.		(26)
CH ₂ OHC(CH ₂ NH ₂) ₃ ·2H ₂ SO ₄	288		(26)
CH ₂ OHC(CH ₂ NH ₂) ₃ ·2H ₂ C ₂ O ₄	172		(26)
CH ₂ OHC(CH ₂ NH ₂) ₃ tripicrate.....	145 d.		(96)
CH ₃ COOCH ₂ C(CH ₂ NHCOCH ₃) ₃	58		(26)
C ₆ H ₅ COOCH ₂ C(CH ₂ NHCOC ₆ H ₅) ₃	231-232		(96)
CH ₂ OHC(CH ₂ NHCOC ₆ H ₄ NO ₂ -o) ₃	229		(96)
CH ₂ OHC(CH ₂ NHCH ₃) ₃		142/15 mm.	(59)
CH ₂ OHC(CH ₂ NHCH ₃) ₃ ·3HCl.....	155 (from methanol); 229 (dried)		(59)
CH ₂ OHC[CH ₂ N(CH ₃) ₂] ₃		125/13 mm.	(59)
CH ₂ OHC[CH ₂ N(CH ₃) ₂] ₃ ·3HCl.....	238		(59)
CH ₂ ClC(CH ₂ NH ₂) ₃			
CH ₂ ClC(CH ₂ NH ₂) ₃ ·3HCl.....	276		(96)
CH ₂ ClC(CH ₂ NH ₂) ₃ tripicrate.....	122		(96)
CH ₂ ClC(CH ₂ NHSO ₂ C ₇ H ₇) ₃	271-272		(96)
CH ₂ BrC(CH ₂ NHSO ₂ C ₇ H ₇) ₃	268		(96)

accomplished with aqueous ammonia at 200°C. to give a 60 per cent yield of the monoamine (XXV).

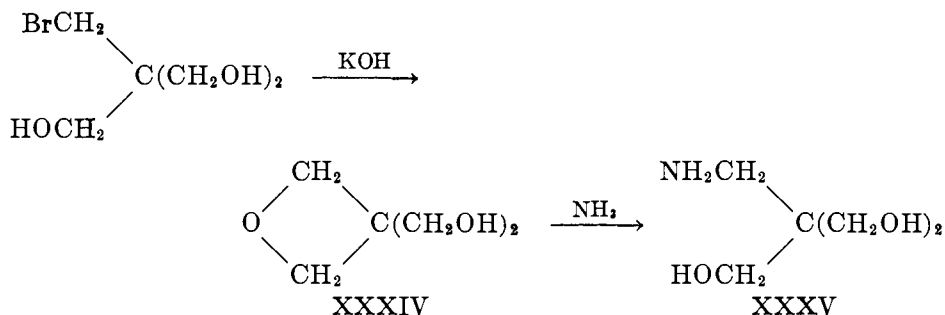


TABLE 15

Derivatives of 2,2-bis(aminomethyl)-1,3-propanediol

COMPOUND	MELTING POINT	BOILING POINT	REFER- ENCE
	°C.	°C.	
$(\text{CH}_2\text{OH})_2\text{C}(\text{CH}_2\text{NH}_2)_2 \cdot \text{H}_2\text{O}$		200/0.002 mm.	(70)
$(\text{CH}_2\text{OH})_2\text{C}(\text{CH}_2\text{NH}_2)_2 \cdot 2\text{H}_2\text{C}_2\text{O}_4$	160 d.		(70)
$(\text{CH}_2\text{OH})_2\text{C}(\text{CH}_2\text{NH}_2)_2 \cdot \text{H}_2\text{CO}_3$	Reverts to diamine at 164		(70)
$(\text{CH}_2\text{OH})_2\text{C}(\text{CH}_2\text{NH}_2)_2$ dipicrate.....	223 d.		(70)
$(\text{HOCH}_2)(\text{BrCH}_2)\text{C}(\text{CH}_2\text{NH}_2)_2$			(73)
$(\text{HOCH}_2)(\text{BrCH}_2)\text{C}(\text{CH}_2\text{NH}_2)_2 \cdot 2\text{HBr}$			(73)
$(\text{BrCH}_2)_2\text{C}(\text{CH}_2\text{NH}_2)_2$			(73)
$(\text{BrCH}_2)_2\text{C}(\text{CH}_2\text{NH}_2)_2 \cdot 2\text{HBr}$	286 d.		(73)
$(\text{CH}_2\text{OH})_2\text{C}(\text{CH}_2\text{NHCH}_3)_2$	40	185/25 mm.	(59)
$(\text{CH}_2\text{OH})_2\text{C}(\text{CH}_2\text{NHCH}_3)_2 \cdot 2\text{HCl}$	198		(59)
$(\text{CH}_2\text{OH})_2\text{C}(\text{CH}_2\text{NHCH}_3)_2 \cdot 2\text{HBr}$	214		(59)
$(\text{CH}_2\text{OH})_2\text{C}[\text{CH}_2\text{N}(\text{CH}_3)_2]_2$	36	160-162/24 mm. 137/15 mm.	(59) (75)
$(\text{CH}_2\text{OH})_2\text{C}[\text{CH}_2\text{N}(\text{CH}_3)_2]_2 \cdot 2\text{HCl}$	208		(59)
$(\text{CH}_2\text{OH})_2\text{C}[\text{CH}_2\text{N}(\text{CH}_3)_2]_2 \cdot 2\text{HBr}$	207		(75)
$(\text{CH}_2\text{OH})_2\text{C}[\text{CH}_2\text{N}(\text{CH}_3)_2]_2$ dipicrate.....	155		(75)
$(\text{CH}_2\text{OH})_2\text{C}[\text{CH}_2\text{N}(\text{CH}_3)_2]_2 \cdot 2\text{CH}_3\text{I}$			(75)
$(\text{CH}_2\text{OH})_2\text{C}[\text{CH}_2\text{N}(\text{CH}_3)_2]_2 \cdot 2\text{CH}_3\text{Br}$	185		(75)
$(\text{CH}_2\text{OH})_2\text{C}[\text{CH}_2\text{N}(\text{CH}_3)_2]_2$ dimethopicrate.....	194		(75)
$(\text{CH}_3\text{COOCH}_2)_2\text{C}[\text{CH}_2\text{N}(\text{CH}_3)_2]_2$	35	151/12 mm.	(75)
$(\text{CH}_3\text{COOCH}_2)_2\text{C}[\text{CH}_2\text{N}(\text{CH}_3)_2]_2 \cdot 2\text{CH}_3\text{I}$	229		(75)
$(\text{CH}_2\text{COOCH}_2)_2\text{C}[\text{CH}_2\text{N}(\text{CH}_3)_2]_2 \cdot 2\text{CH}_3\text{Br}$	228 d.		(75)
$(\text{CH}_2\text{COOCH}_2)_2\text{C}[\text{CH}_2\text{N}(\text{CH}_3)_2]_2$ dimetho- picrate.....	184-185		(75)
$(\text{CH}_2\text{COOCH}_2)_2\text{C}[\text{CH}_2\text{N}(\text{CH}_3)_2]_2$ dimetho- perchlorate.....	272 d.		(75)
$(\text{C}_6\text{H}_5\text{COOCH}_2)_2\text{C}[\text{CH}_2\text{N}(\text{CH}_3)_2]_2 \cdot 2\text{HCl}$	244		(59)
$(\text{C}_6\text{H}_5\text{CHCOOCH}_2)_2\text{C}[\text{CH}_2\text{N}(\text{CH}_3)_2]_2 \cdot 2\text{HCl}$	212		(59)
$(\text{CH}_2\text{OH})_2 \left(\begin{array}{c} \text{OCOCH}_3 \\ \\ \text{CCH}_2\text{N} \begin{array}{c} \text{CH}_2\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \\ \\ \text{CH}_2\text{CH}_2 \end{array} \right)_2$	84	198/4.5 mm.	(59)
$(\text{CH}_2\text{OH})_2\text{C}[\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2]_2$		160/15 mm.	(59)

Barbiere and Matti (21) have prepared dimethylaminomethyltris(hydroxymethyl)methane directly from the monobromide and dimethylamine. Derivatives of the monoamine are listed in table 16.

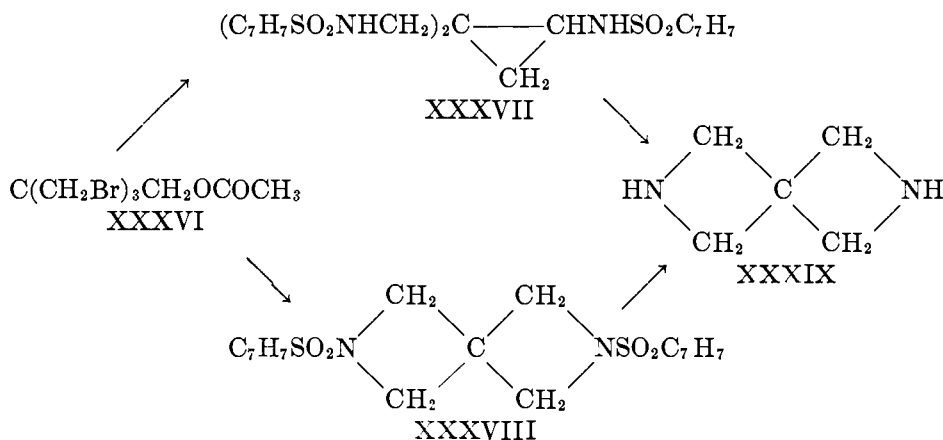
IX. 2,6-DIAZASPIRO[3.3]HEPTANE AND TRIMETHYLENIMINE DERIVATIVES

Litherland and Mann (96) have studied the action of sodium *p*-toluenesulfonamide on tris(bromomethyl)acetoxymethylmethane (XXXVI) at 180°C. and found that two compounds could be isolated: 1-*p*-toluenesulfonamido-2,2-bis(*p*-toluenesulfonamidomethyl)cyclopropane (XXXVII) and *N,N'*-di-*p*-toluenesulfonyl-2,6-diazaspiro[3.3]heptane (XXXVIII). When the tritoluenesulfonamido compound was hydrolyzed with hydrochloric acid, made alkaline, and steam distilled, ammonia and diazaspiroheptane (XXXIX) were pro-

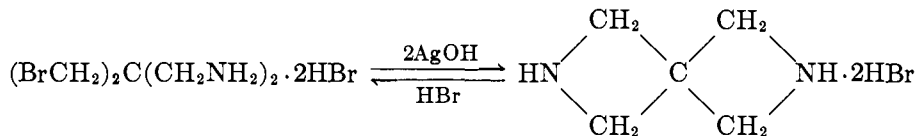
TABLE 16
Derivatives of aminomethyltris(hydroxymethyl)methane

COMPOUND	MELTING POINT	BOILING POINT	REFERENCE
	°C.	°C.	
(HOCH ₂) ₃ CCH ₂ NH ₂	207		(71)
[(HOCH ₂) ₃ CCH ₂ NH ₂] ₂ ·H ₂ C ₂ O ₄	206		(71)
(HOCH ₂) ₃ CCH ₂ NH ₂ picrate.....	80		(71)
(CH ₃ COOCH ₂) ₃ CCH ₂ NHCOCH ₃		173/0.04 mm.	(71)
(HOCH ₂) ₃ CCH ₂ NHCOOH·NH ₂ CH ₂ C(CH ₂ OH) ₃	149 d.		(71)
(HOCH ₂) ₃ CCH ₂ N(CH ₃) ₂	51-52	178-182/4 mm.	(21)
(HOCH ₂) ₃ CCH ₂ N(CH ₃) ₂ ·HCl.....	125.5		(21)

duced, the latter in low yield. When the ditoluenesulfonyl compound was treated similarly, the same spirocyclic compound was obtained in higher yield.



Govaert and Beyaert (73) found that the dihydrobromide of 2,6-diazaspiro-[3.3]heptane was formed when 2 molecules of hydrogen bromide were removed with silver oxide from the dihydrobromide of 2,2-bis(bromomethyl)-1,3-diaminopropane; the reaction was reversed with 66 per cent hydrobromic acid at 180°C.



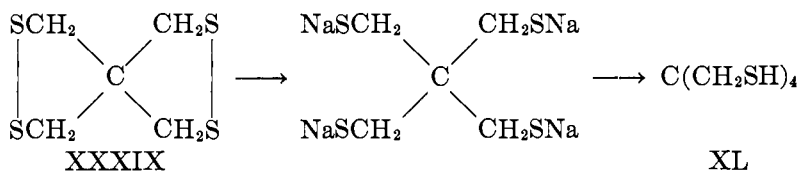
They attempted to isolate the spiro base in the free state, but found that polymerization always occurred.

Derivatives of 2,6-diazaspiro[3.3]heptane and of trimethylenimine which have been prepared from pentaerythritol are listed in table 17.

X. SULFUR-CONTAINING PENTAERYTHRITOL DERIVATIVES

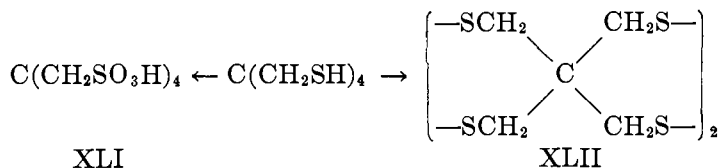
A. *Tetrakis(mercaptomethyl)methane*

The tetrathio derivative of pentaerythritol, tetrakis(mercaptomethyl)methane (XL), has been prepared by Backer and Evenhuis (11) by the reduction of 2,3,7,8-tetrathiaspiro[4.4]nonane (XXXIX) (see page 193) 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 (54) from the polymeric product obtained by the action of sodium tetrasulfide on pentaerythrityl tetrabromide, by hydrogenation in dioxane solution over a cobalt polysulfide catalyst.

Tetrakis(mercaptomethyl)methane is a solid, m.p. 73–73.5°C., which gives solid mercaptides with many heavy metals, and on oxidation with hydrogen peroxide in acetic acid gives the corresponding tetrasulfonic acid (XLI). Oxidation of the sodium derivative with iodine is reported to give a dimer (XLII).



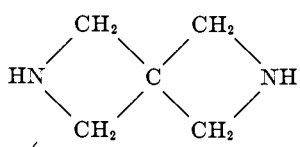
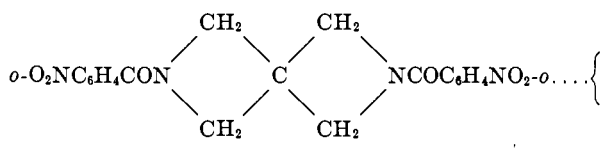
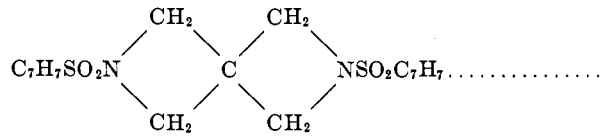
The tetramercaptan condenses readily with aldehydes and ketones in the presence of hydrochloric acid to give solid derivatives of 2,4,8,10-tetrathiaspiro-

TABLE 17

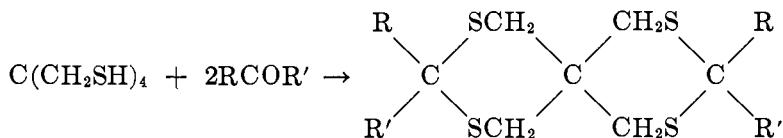
Trimethylenimine derivatives prepared from pentaerythritol, and 2,6-diazaspiro [3.3]heptane derivatives

COMPOUND	MELTING POINT	REFERENCE
$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{HN} \quad \text{C}(\text{CH}_2\text{NH}_2)_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array} \dots\dots\dots$	°C.	(96)
$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{HN} \quad \text{C}(\text{CH}_2\text{NH}_2)_2 \cdot 3\text{HCl} \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array} \dots\dots\dots$	272	(96)
$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{HN} \quad \text{C}(\text{CH}_2\text{NH}_2)_2 \text{ tripicrate} \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array} \dots\dots\dots$	212–213 d.	(96)
$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ o\text{-NO}_2\text{C}_6\text{H}_4\text{CON} \quad \text{C}(\text{CH}_2\text{NHCOC}_6\text{H}_4\text{NO}_2\text{-}o)_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array} \dots\dots\dots$	285	(96)
$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{C}_7\text{H}_7\text{SO}_2\text{N} \quad \text{C}(\text{CH}_2\text{NHSO}_2\text{C}_7\text{H}_7)_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array} \dots\dots\dots$	214	(96)
$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{C}_7\text{H}_7\text{SO}_2\text{N} \quad \text{C}[\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_5)\text{SO}_2\text{C}_7\text{H}_7]_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array} \dots\dots\dots$	181	(96)
$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{I}(\text{CH}_3)_2\text{N} \quad \text{C}[\text{CH}_2\text{N}(\text{CH}_3)_2]_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array} \dots\dots\dots$	208–208.5 d.	(64)
$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{I}(\text{CH}_3)_2\text{N} \quad \text{C} \begin{array}{l} \diagup \quad \text{CH}_2\text{N}(\text{CH}_3)_2\text{I} \\ \diagdown \quad \text{CH}_2\text{N}(\text{CH}_3)_2 \end{array} \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array} \dots\dots\dots$	123–124 d.	(64)

TABLE 17—*Concluded*

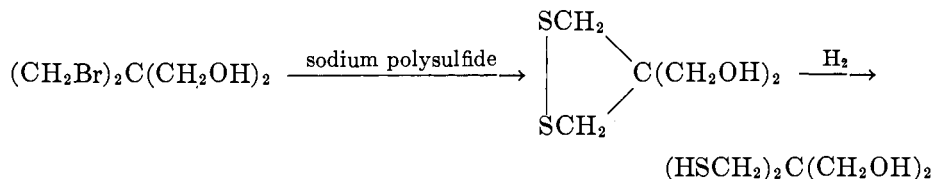
COMPOUND	MELTING POINT	REFERENCE
	°C.	
		(73, 96)
{ ·2HCl	{ 197	{ (73)
·2HBr	275 d.	(96)
Dipicrate	196	(73)
	{ 259	{ (73)
	243 d.	(96)
	218 232	(96) (73)
	186	(73, 96)

[5.5]undecane; condensation with ketones, such as 1,4-cyclohexanedione, is claimed (86) to give linear polymers suitable for bristles, etc.



The corresponding sulfones of some of these derivatives have been prepared by oxidation with hydrogen peroxide in acetic acid.

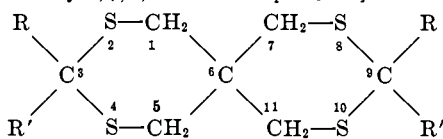
Peppel and Signaigo (120) have reacted sodium polysulfide with pentaerythrityl dibromide to obtain 4,4-dimethylol-1,2-dithiacyclopentane (m.p. 129–130°C.), and by hydrogenation of this compound over a cobalt sulfide catalyst they produced the dithio derivative of pentaerythritol (m.p. 97°C.).



The derivatives of 2,4,8,10-tetrathiaspiro[5.5]undecane which have been prepared from tetrakis(mercaptomethyl)methane are listed in table 18.

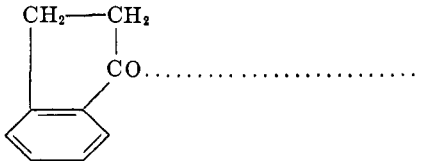
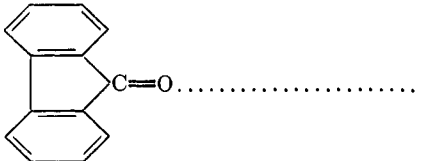
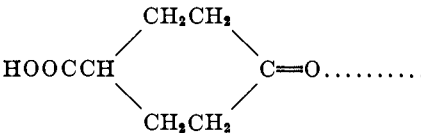
TABLE 18

Derivatives of 2,4,8,10-tetrathiaspiro[5.5]undecane (11)



REAGENT	DERIVATIVE	MELTING POINT
		°C.
CH ₃ CHO.....	3,9-Dimethyl-	110
CH ₃ COCOCH ₃	3,9-Dimethyl-3,9-diacetyl-	164-165.5
.....	3,9-Difuryl-	132.5-133
CH ₃ COCH ₃	3,3,9,9-Tetramethyl- 3,3,9,9-Tetramethyl tetrasulfone	192-193
CH ₃ COCH ₂ CH ₃		>350
(CH ₃ CH ₂) ₂ CO.....	3,9-Dimethyl-3,9-diethyl- 3,3,9,9-Tetraethyl- 3,3,9,9-Tetraethyl tetrasulfone	143-143.5
CH ₃ COC(CH ₃) ₃		118-118.5
CH ₃ CH ₂ COC(CH ₃) ₃	3,9-Dimethyl-3,9-di- <i>tert</i> -butyl-	165-167
	3,9-Diethyl-3,9-di- <i>tert</i> -butyl-	177-178
.....	3,9-Bis(tetramethylene)- 3,9-Bis(tetramethylene) tetra- sulfone	212.5-213
		>300
.....	3,9-Bis(pentamethylene)- 3,9-Bis(pentamethylene) tetra- sulfone	206-207
		>300
.....	3,9-Bis(thiodiethylene)-	273
C ₆ H ₅ CHO.....	3,9-Diphenyl-	233-234
<i>p</i> -CH ₃ C ₆ H ₄ CHO.....	3,9-Di- <i>p</i> -tolyl-	244-245
Vanillin.....	3,9-Bis(4-hydroxy-3-methoxy- phenyl)-	269-271
Piperonal.....	3,9-Bis(3,4-methylenedioxy- phenyl)	265-267
C ₆ H ₅ CH=CHCHO.....	3,9-Bis(2-phenylethenyl)-	225-226
C ₆ H ₅ COCH ₃	3,9-Dimethyl-3,9-diphenyl-	184-185
(C ₆ H ₅) ₂ CO.....	3,3,9,9-Tetraphenyl-	222-223

TABLE 18—Concluded

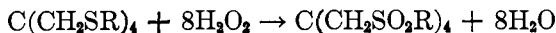
REAGENT	DERIVATIVE	MELTING POINT °C.
		258–259
		> 300
		

B. Thio ethers, sulfoxides, and sulfones

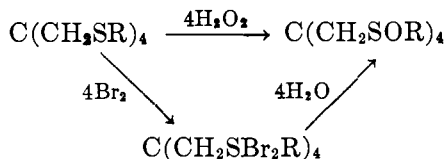
Thio ethers derived from pentaerythritol have been prepared by Backer and Dijkstra (6) and Backer, Terpstra, and Dijkstra (18) by the reaction of pentaerythrityl tetrabromide with the sodium derivative of the corresponding mercaptan or thiophenol, generally at about 150°C.



The thio ethers are readily oxidized with hydrogen peroxide in acetic acid to give the corresponding sulfones. The oxidation can also be effected with nitric acid or with potassium permanganate in acetone (7).

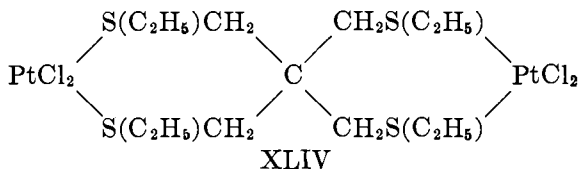
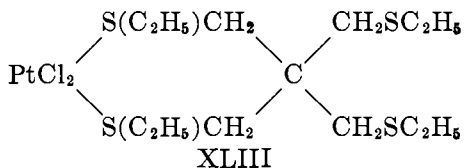


Backer and Dijkstra (8) have prepared the corresponding sulfoxides from the thio ethers by oxidation with the theoretical quantity of hydrogen peroxide or by hydrolysis of their octabromides.



The thio ethers form addition compounds with mercuric chloride, generally with 2 molecules, although certain thio ethers combine with 4 molecules. Ischugajeff and Iljin (147) have reported that pentaerythrityl tetraethyl thio ether gives two products on reaction with potassium chloroplatinate. In the cold, the

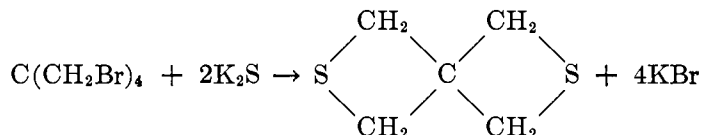
compound XLIII is obtained, and if the reactants are heated, a mixture of XLIII with XLIV results.



The thio ethers, sulfoxides, and sulfones derived from pentaerythritol, and their derivatives, are listed in table 19.

C. 2,6-Dithiaspiro[3.3]heptane

Backer and Keuning (12, 13) have found that 2,6-dithiaspiro[3.3]heptane (XLV) is prepared readily by the action of excess potassium sulfide on pentaerythrityl tetrabromide in alcoholic solution. It has been prepared similarly by Kravets (93).



When an insufficiency of potassium sulfide was employed, there was produced only this dithio ether, with no evidence of the monocyclic compound. Theoretically there are five possible oxidation products from this dithio ether, and all have been prepared by Backer and Keuning from it. With potassium permanganate and hydrogen peroxide in excess, the disulfone (XLVI) was readily obtained; with 3 moles of hydrogen peroxide, the sulfoxide-sulfone (XLVII) resulted; and 2 moles of hydrogen peroxide or nitric acid or an excess of chromic acid produced the disulfoxide (XLVIII).

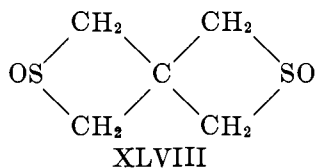
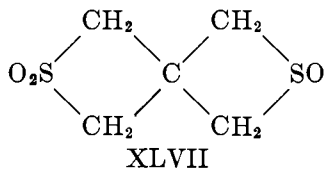
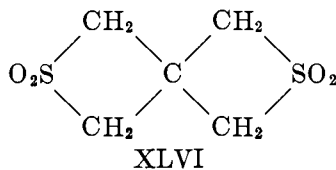


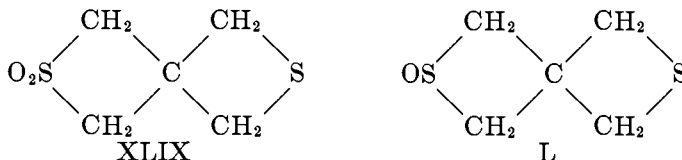
TABLE 19

Thio ethers, sulfoxides, and sulfones derived from pentaerythritol

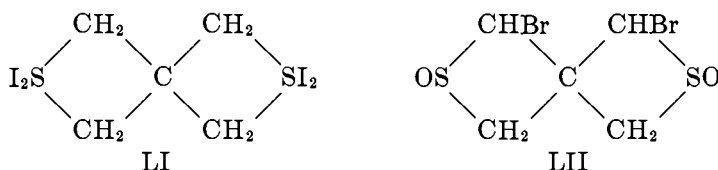
PENTAERYTHRITYL	THIO ETHER (6, 18)		THIO ETHER OCTABROMIDE (8)	THIO ETHER-HgCl ₂ ADDUCT (8)	SULFOX- IDE (8)	SULFONE (7, 8)
	Melting point	Boiling point	Melting point	Melting point	Melting point	Melting point
	°C.	°C.	°C.	°C.	°C.	°C.
Tetramethyl.....	-1	209-211/15 mm.	107 d.	+2HgCl ₂ 143	205	Decomposes >300
Tetracthyl.....		218-220/15 mm.*	93 d.	+2HgCl ₂ 157.5	137	185.5
Tetra- <i>n</i> -propyl.....		222-225/2 mm.	80 d.	+2HgCl ₂ 88	117	126.5
				+4HgCl ₂ 141		
Tetraisopropyl.....		192-193/2 mm.	80 d.		165	220.5
Tetraallyl.....		214-217/2 mm.				
Tetra- <i>n</i> -butyl.....		226-230/2 mm.		+HgCl ₂ 51	123	111.5
				+2HgCl ₂ 97		
				+4HgCl ₂ 149		
Tetraisobutyl.....		206-208/2 mm.				134
Tetra- <i>sec</i> -butyl.....		221-223/2 mm.				115
Tetra- <i>tert</i> -butyl.....	123.6		130 d.	+2HgCl ₂ Decom- poses >300	212	Decomposes >300
				+2HgCl ₂ 84		
				+4HgCl ₂ 128	143	83.5
Tetra- <i>n</i> -amyl.....		241-243/2 mm.			159.5	85.5
Tetra- <i>n</i> -hexyl.....		206-208/10 ⁻⁵ mm.				72
Tetra- <i>n</i> -heptyl.....		222-224/10 ⁻⁵ mm.				80
Tetra- <i>n</i> -octyl.....		238-240/10 ⁻⁵ mm.				76
Tetra- <i>n</i> -nonyl.....		251-253/10 ⁻⁵ mm.				78.8
Tetra- <i>n</i> -decyl.....	19	259-261/10 ⁻⁵ mm.				72.5
Tetra- <i>n</i> -undecyl.....	28					78.3
Tetra- <i>n</i> -dodecyl.....	35-36					244
Tetraphenyl.....	86					328
Tetra- <i>p</i> -bromophenyl.....	110					276
Tetra- <i>p</i> -chlorophenyl.....	96					249
Tetra- <i>p</i> -tolyl.....	103					179.5
Tetrabenzyl.....	73					183
Tetraphenylethyl.....						

* Reference 147.

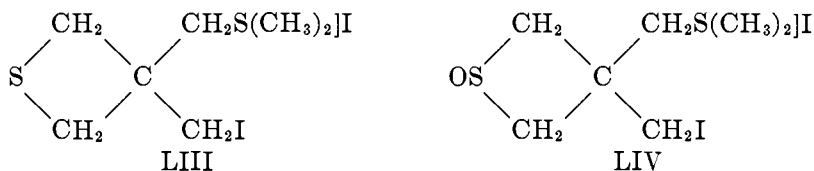
The monosulfone (XLIX) was prepared by the reduction of the sulfoxide-sulfone (XLVII), and the monosulfoxide (L) was prepared by oxidation of the dithio ether with 1 mole of hydrogen peroxide or with chromic acid in acetic acid.



The dithio ether unites with iodine to form the tetraiodide (LI), and reacts with bromine to give a compound which on hydrolysis produces 1,5-dibromo-2,6-dithiaspiro[3.3]heptane-2,6-dioxide (LII). The tetrabromide was obtained as a viscous oil by reaction of the dithio ether with bromine vapor.



The dithio ether combines with mercuric chloride. It unites with methyl iodide to form a compound which is probably LIII, as only one iodine atom is ionized. The monosulfoxide also reacts with 2 molecules of methyl iodide to form a similar compound (LIV).

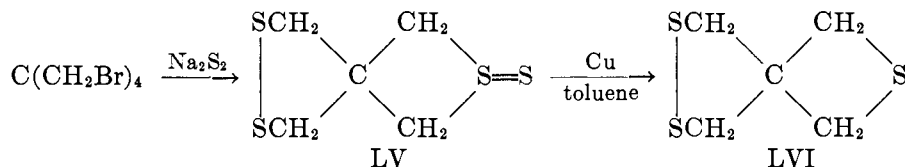


The disulfoxide forms addition compounds with many salts and it has been resolved through its addition compound with cobalt *d*-camphorsulfonate.

2,6-Dithiaspiro[3.3]heptane and its derivatives are listed in table 20.

D. 2,6,7-Trithiaspiro[3.4]octane

Backer and Evenhuis (9) have shown that by the reaction of sodium or potassium disulfide with pentaerythrityl tetrabromide in boiling ethanol, 2-thio-2,6,7-trithiaspiro[3.4]octane (LV) is produced, and when this is boiled with copper in toluene it is converted to 2,6,7-trithiaspiro[3.4]octane (LVI).



Oxidation of 2-thio-2,6,7-trithiaspiro[3.4]octane with perbenzoic acid gave 2,6,7-trithiaspiro[3.4]octane-2,2,6,6-tetraoxide (LVII), and when hydrogen

TABLE 20

2,6-Dithiaspiro[3.3]heptane and its derivatives

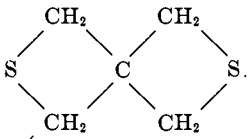
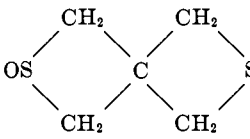
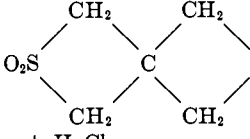
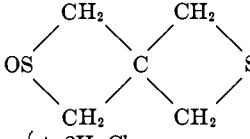
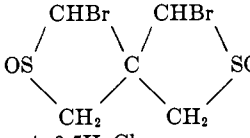
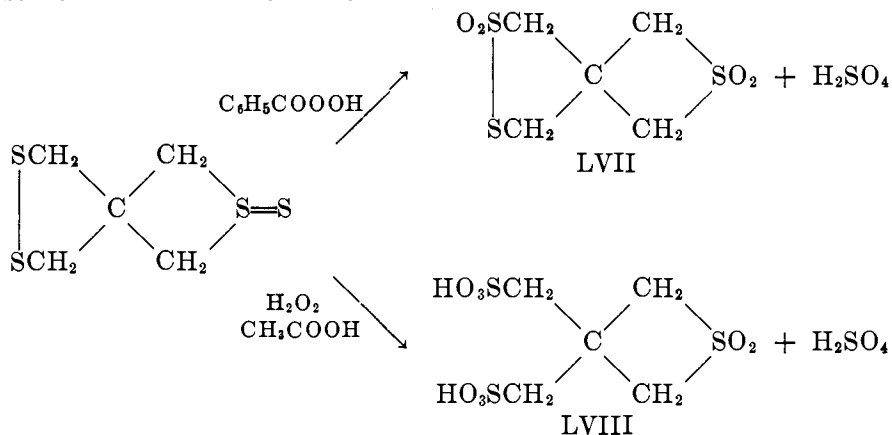
COMPOUND	MELTING POINT °C.	BOILING POINT °C.	REFERENCE
	31.5	108-109/16 mm. 116-118/15 mm.	(12) (93)
+ 2HgCl ₂	Decomposes	Viscous oil	(12)
+ 2Br ₂	Decomposes about 100		(13)
+ 2I ₂			(12)
	81.5		(12)
+ 1.5HgCl ₂	Decomposes		(12)
	116.5		(12)
+ HgCl ₂	177-178		(12)
	146		(12)
+ 2HgCl ₂	185 d.		(12)
+ 0.5CuCl ₂		(13)	
+ CuCl ₂		(13)	
+ CaCl ₂		(13)	
+ MnCl ₂		(13)	
+ 0.5NiCl ₂		(13)	
+ 0.5CoCl ₂		(13)	
+ 1.33CdCl ₂		(13)	
+ H ₂ PtCl ₆	(13)		
	126.5		(12)
+ 0.5HgCl ₂	120 d.		(13)

TABLE 20—*Concluded*

COMPOUND	MELTING POINT	BOILING POINT	REFERENCE
	°C.	°C.	
	156		(12)
+ HgCl ₂	186-187 d.		(12)
	244.5 136-137		(12) (93)
	143 d. 135		(12, 13, 93)
	133-134		(13)

peroxide in acetic acid was used as the oxidizing agent 1-thia-3,3-disulfodimethylcyclobutane-1,1-dioxide (LVIII) was produced; a molecule of sulfuric acid was also isolated from each oxidation.



Derivatives of 2,6,7-trithiaspiro[3.4]octane which have been prepared from pentaerythritol are listed in table 21.

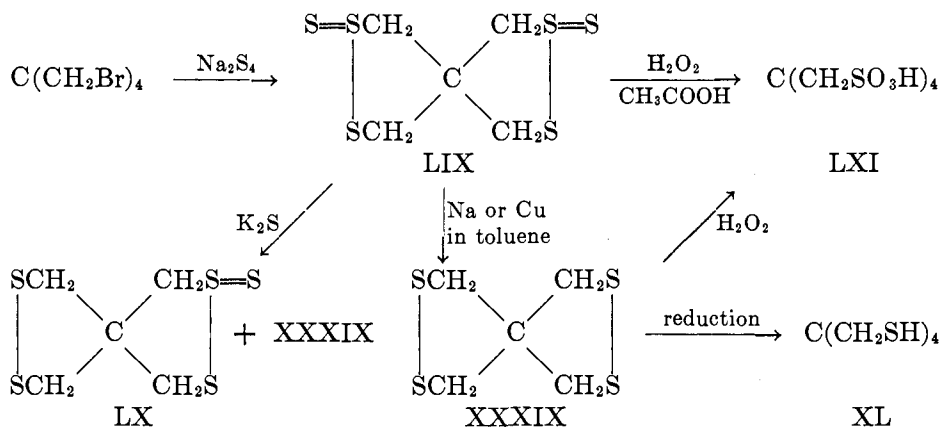
E. 2,3,7,8-Tetrathiaspiro[4.4]nonane

The reaction of pentaerythrityl tetrabromide with sodium tetrasulfide in boiling alcohol has also been examined by Backer and Evenhuis (10), and a product has been isolated which is probably 2,7-dithio-2,3,7,8-tetrathia-

TABLE 21
Derivatives of 2,6,7-trithiaspiro[3.4]octane

COMPOUND	MELTING POINT	REFERENCE
	°C.	
	78.5	(9)
{ + HgCl ₂		(9)
{ + HgBr ₂		(9)
	55.5-56.5	(9)
	257 d.	(9)
		(9)
	144-146 d.	(9)
	200-202	(9)

spiro[4.4]nonane (LIX). Reaction of this hexasulfide with sodium or copper in boiling toluene produced 2,3,7,8-tetrathiaspiro[4.4]nonane (XXXIX), and reaction with potassium sulfide in boiling alcohol gave 2-thio-2,3,7,8-tetrathiaspiro[4.4]nonane (LX), together with some of the tetrasulfide (XXXIX).

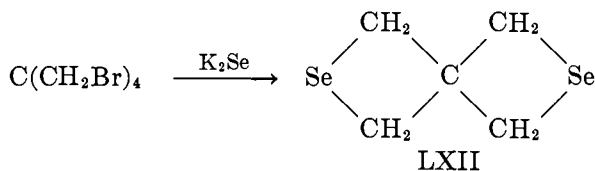


Reduction of the tetrasulfide (XXXIX) with sodium in liquid ammonia (11) produced tetrakis(mercaptomethyl)methane (XL) (see page 182), and oxidation of the hexasulfide (LIX) or the tetrasulfide (XXXIX) with hydrogen peroxide in acetic acid gave tetramethylmethanetetrasulfonic acid (LXI).

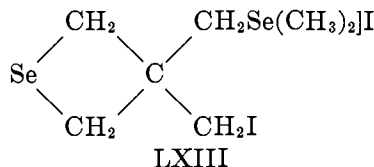
Derivatives of 2,3,7,8-tetrathiaspiro[4.4]nonane which have been prepared from pentaerythritol are shown in table 22.

XI. 2,6-DISELENASPIRO[3.3]HEPTANE

By the reaction of potassium selenide with pentaerythrityl tetrabromide in an inert atmosphere, Backer and Winter (19) have prepared 2,6-diselenaspiro[3.3]heptane (LXII).



This substance is readily oxidizable, and forms an addition compound with mercuric chloride; its 2,2,6,6-tetraiodo derivative is unstable. Reaction with 2 molecules of methyl iodide produces 3-iodomethyl-3-methylselenomethyl-1-selenacyclobutane methiodide (LXIII).



The derivatives of 2,6-diselenaspiro[3.3]heptane which have been prepared from pentaerythritol are listed in table 23.

XII. COMPOUNDS WITH ARSENIC AND BORON

Englund (51) suggested that reaction took place between pentaerythritol and arsenic derivatives, because of the observed increased solubility of the arsenic

TABLE 22
2,3,7,8-Tetrathiaspiro[4.4]nonane derivatives

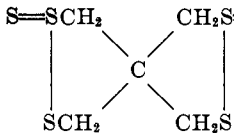
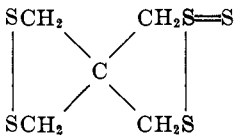
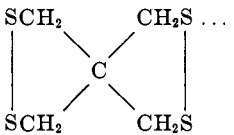
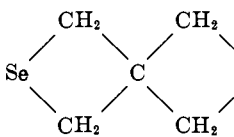
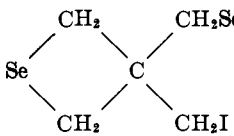
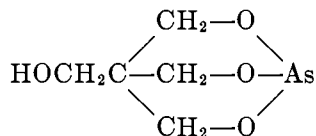
COMPOUND	MELTING POINT °C.	REFERENCE
	182-184	(10)
	117.5-118	(10)
	80-80.5	(10)
{ + HgCl ₂	132	
{ + HgBr ₂	127-127.5	
C(CH ₂ SO ₂ H) ₄		(10)
C(CH ₂ SO ₂ Cl) ₄	217 d.	(10)

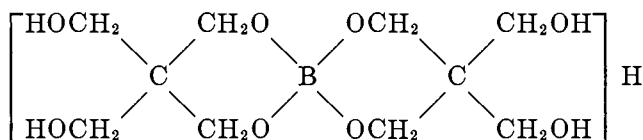
TABLE 23
Derivatives of 2,6-diselenaspiro[3.3]heptane

COMPOUND	MELTING POINT °C.	REFERENCE
	67	(19)
{ + 2HgCl ₂		(19)
{ + 2I ₂		(19)
	112-113	(19)
Picrate.....	113-113.5	

derivative in glacial acetic acid when pentaerythritol was present. By heating together pentaerythritol and arsenious oxide (52) he isolated a crystalline compound C₅H₉O₄As, m.p. 102-103°C., probably having the following structure:



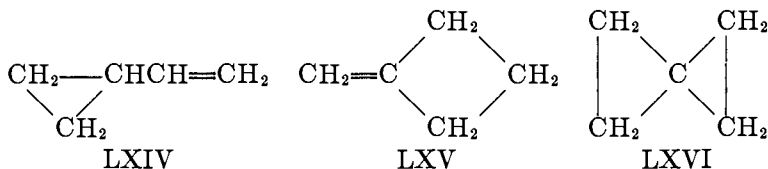
Orthner and Freyss (119) have examined the specific conductivity of boric acid in the presence of pentaerythritol and its derivatives. No increase in conductivity was observed by the addition of the monoisopropylidene derivative of pentaerythritol, pentaerythryl dimethyl ether, or pentaerythryl dibenzoate, but pentaerythritol itself was found to cause an increase in conductivity and this was ascribed to the formation of the compound:



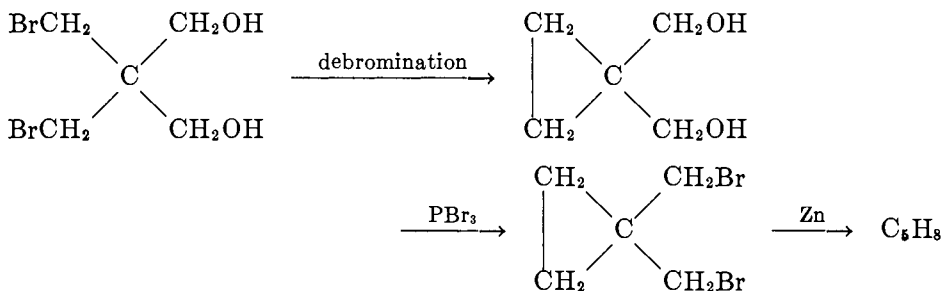
XIII. SPIRANES

The products of the debromination of pentaerythryl tetrabromide have attracted a considerable number of workers, and there are many conflicting statements in their publications.

Gustavson (78) first debrominated pentaerythryl tetrabromide with zinc. He assigned to the reduction product the structure of vinyltrimethylene (LXIV), although later (79) he suggested that methylenecyclobutane (LXV) was possibly more likely. Fecht (56) concluded that the product was spiropentane (LXVI).



Demjanov (45) favored the methylenecyclobutane structure and Zelinski (157), who did his debromination in two stages, concluded that the spirocycloane structure would more nearly account for the chemical reactions and synthesis of the compound.



Favorski and Batalin (55) decided that Gustavson's "vinyl trimethylene" was methylenecyclobutane, and Filipov (61) said that the reduction product was a mixture of methylenecyclobutane and methylcyclobutene.

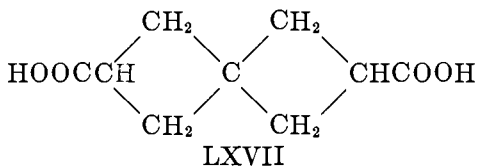
Merezhkovskii (106) repeated Fecht's work and concluded that the allocation of the spirocycloane structure was not justified by the evidence, and Demjanov and Dojarenko (46) in 1922 preferred methylenecyclobutane. Ingold in 1923 (87) was unable to isolate any spiro-pentane from the reduction product. Rogowski (129) interpreted the results of an electron diffraction study on the reduction product as being consistent with the spiro-pentane structure.

Williams (154) has prepared cyclobutane derivatives by the debromination of pentaerythrityl tetrabromide with zinc and it is recorded (153) that Whitmore and Philips, by debromination with zinc, obtained a mixture shown by ozonolysis to consist of methylenecyclobutane and 2-methyl-1-butene with no evidence of other compounds.

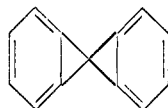
Bauer and Beach (23) made an electron diffraction study of the high-boiling fraction obtained by Whitmore and Williams and concluded that it was methylenecyclobutane and not spiro-pentane. Murray and Stevenson (110) in 1944, by Raman spectroscopic examination, found that the product of the debromination of pentaerythrityl tetrabromide with zinc in aqueous methanol consisted of methylenecyclobutane, 2-methyl-1-butene and a small quantity of a compound considered to be spiro-pentane. When reduction was carried out with zinc in molten acetamide in the presence of sodium iodide and sodium carbonate, they obtained the same mixture, but with the spiro-pentane fraction in 40 per cent yield. It is recorded that the spiro-pentane fraction was chemically stable. Donohue, Humphrey, and Schomaker (47) have confirmed the structure of this compound as spiro-pentane by electron diffraction studies. Slabey (142) carried out a debromination of pentaerythrityl tetrabromide in ethanol with zinc in the presence of sodium iodide and sodium carbonate. He obtained a higher yield of hydrocarbon products (78-89 per cent) than Murray and Stevenson, and these were found to consist of methylenecyclobutane (54-58 per cent), spiro-pentane (24-28 per cent), 2-methyl-1-butene (13-18 per cent), and 1,1-dimethylcyclopropane (1-3 per cent).

Shand, Schomaker, and Fischer (138) have carried out electron diffraction studies of methylenecyclobutane which they isolated from the debromination of pentaerythrityl tetrabromide. From the reaction product they could not isolate any methylcyclobutene.

Fecht (56) reported the preparation of spiro[3.3]heptane-2,5-dicarboxylic acid (LXVII) and the corresponding 2,2,5,5-tetracarboxylic acid from pentaerythrityl tetrabromide and malonic ester. The dicarboxylic acid has also been prepared by Backer and Schurink (15) and has been resolved by them.



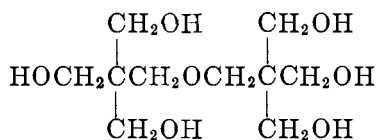
Fecht (56) caused benzene, aluminum chloride, and pentaerythrityl tetrabromide to react, and obtained two hydrocarbons in poor yield. The structure LXVIII was not ascribed to either.



LXVIII

XIV. DIPENTAERYTHRITOL

Dipentaerythritol (LXIX) is the ether derived from 2 molecules of pentaerythritol by elimination of 1 molecule of water.



LXIX

There is no record of its synthesis from pentaerythritol, and its only known preparation is as a by-product in the manufacture of pentaerythritol. It is present in varying amounts in commercial pentaerythritol, generally of the order of 5 per cent or less.

The separation of dipentaerythritol from large quantities of pentaerythritol by crystallization from water is difficult on account of their similar solubilities, and also on account of the formation of double compounds. For example, the double compound $(\text{CH}_2\text{OH})_3\text{CCH}_2\text{OCH}_2\text{C}(\text{CH}_2\text{OH})_3 \cdot 4\text{C}(\text{CH}_2\text{OH})_4$, m.p. 185–190°C., crystallizes unchanged from hot water, and is not split into its components below 108°C. (156). It has been claimed (99) that a considerable separation of dipentaerythritol from pentaerythritol can be effected by applying a wet-sieving or scouring process to the crude pentaerythritol synthesis product, because of differing particle sizes. Bried (37) has claimed that by altering the conditions of the pentaerythritol synthesis, a product can be obtained which contains as much as 35–40 per cent of dipentaerythritol. Friederich and Brün (62) have prepared pure dipentaerythritol by separating a mixture of pentaerythritol tetranitrate and dipentaerythritol hexanitrate by their differing solubilities in acetone, followed by saponification. The chromatographic separation of a small amount of dipentaerythritol from a large amount of pentaerythritol has been reported by Lew, Wolfrom, and Goepf (94).

A few derivatives of dipentaerythritol have been prepared, and these are listed in table 24. Friederich and Brün (62) record that dipentaerythritol hexaformate eliminated carbon monoxide at 270°C. to give dipentaerythritol almost quantitatively, and that the hexatryl ether of dipentaerythritol is readily decomposed by water. From the oxidation of dipentaerythritol with nitric acid they isolated a polymerization product of diglycolic aldehyde, $\text{O}(\text{CH}_2\text{CHO})_2$.

XV. HIGHER POLYPENTAERYTHRITOLS

Burrell (43) has stated that tripentaerythritol, m.p. 242–248°C., has been isolated from the pentaerythritol synthesis by-products and that its structure has been proved to be LXX, but so far this work has not been published.

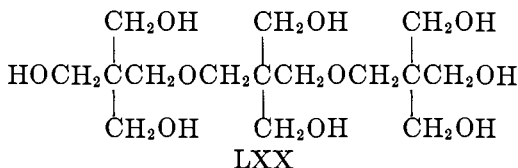


TABLE 24

Derivatives of dipentaerythritol

COMPOUND	MELTING POINT	BOILING POINT	REFERENCE
	°C.	°C.	
Dipentaerythritol.....	221		(62)
Dipentaerythritol hexaformate.....	56		(62)
Dipentaerythritol hexaacetate.....	73		(62)
Dipentaerythritol hexapropionate.....		240–250/2 mm.	(158)
Dipentaerythritol triacetate tripropionate...		Viscous liquid	(22)
Dipentaerythritol hexabutyrate.....	15–20		(158)
Dipentaerythritol hexabenzozoate.....	183		(62)
Dipentaerythritol hexanitrate.....	75		(62)
Dipentaerythritol diiodohydrin.....	106–107		(62)
Dipentaerythritol hexabutyl ether.....	173		(62)
Dipentaerythritol allyl ethers:.....			
4.6 Allyl groups.....		174/0.3 mm.	(115)
Hexaallyl.....		184–186/1 mm.	(115)
Dipentaerythritol methallyl ethers:			
4.6 Methallyl groups.....		200–205/0.8 mm.	
Hexamethallyl.....		183–185/0.3 mm.	(115)

Wyler (155) has nitrated tripentaerythritol and obtained the octanitrate, m.p. 82–84°C., which is claimed to be a useful explosive.

A mixture of polypentaerythritols of m.p. 230–240°C. which is obtained from the pentaerythritol by-products approximates closely to tripentaerythritol and has been named pleopentaerythritol. It is considered by Burrell (43) to be a mixture of di- and tri-pentaerythritols with probably some tetrapentaerythritol.

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