CHEMICAL PROPERTIES AND DERIVATIVES OF GLYCERINE

Chemical Properties and Derivatives of Glycerol

Introduction

This booklet is the second in a series, the first being "Physical Properties of Glycerine and its Solutions," published in 1963. Together, they present the more important available data on this versatile chemical compound.

One of the significant things about glycerine is the scientific background which history has contributed to its properties and reactions — extending over far more years and into more obscure corners of research and technology than any comparable, newly synthesized organic chemical. The chemical reactions of glycerine *as an article of commerce* are relatively simple, and it is these with which this review is primarily concerned. At the same time, we have covered many reactions of historical or scientific interest which have no current commercial significance. We have not attempted to cover all the complexities of physiological reactions in which glycerine and its derivatives as natural components of life processes are involved, even though new analytical techniques are opening up many new findings in this area.

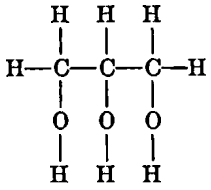
Industrially, the classic glycerine derivative, glycerol tri-nitrate, has gradually lost its dominance. Alkyd resins derived from glycerine represent the greatest single use of chemically combined glycerine today. In the toilet goods and food fields, the esters of glycerine, particularly the partial esters (mono- and di-glycerides) have become highly specialized components of emulsified products, contributing control over the softness and "spreadability" of everything from make-up to margarine.

In a third booklet in this series, also now available, applications — new and old — growing out of the unique combination of physical and chemical properties of glycerine have been covered.

CHARACTERISTICS & NOMENCLATURE

Glycerol is the simplest trihydric alcohol. It is considered to be a derivative of propane and is called 1,2,3-propanetriol. It is colorless, viscous at room temperature, and odorless when pure, has a warm sweet taste and is neutral to indicators.

Its empirical formula $C_3H_8O_3$ indicates the molecular weight 92.09, and its structural formula shows it to have two primary and one secondary hydroxyl. The

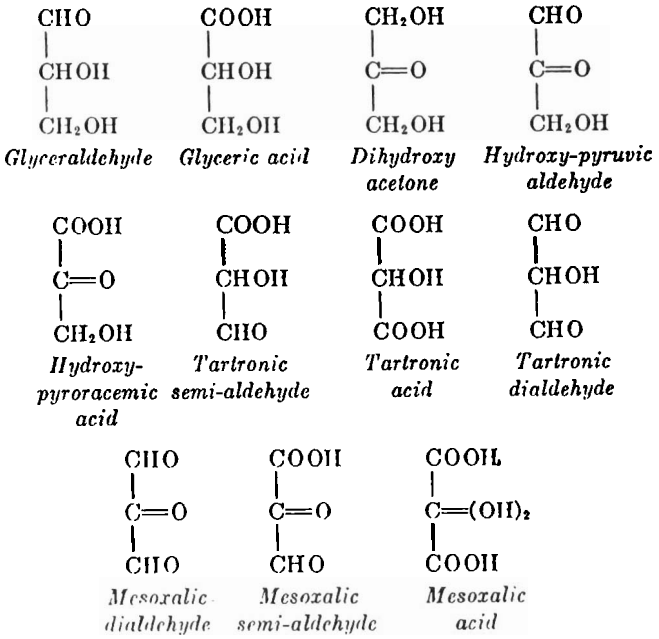


hydroxyl hydrogens are replaceable by metals to form glyceroxides, by acid groups to form esters and by alkyl and aryl radicals to form ethers.

Its chemical nature is that of the alcohols, but because of the multiple hydroxyl groups, it possesses possibilities for more than the usual number of reactions and derivatives. The primary hydroxyls are usually more reactive than the secondary group, and the first one to react does so more readily than the second. However, this generalization does not always hold. For example the glycerol β-formate is formed more readily than the alpha isomer. Although one hydroxyl may be more reactive than another, there is generally some reaction of the second and third hydroxyls before all of the most reactive ones have been utilized. Consequently, glycerol derivatives are obtained as mixtures containing isomers and products of different degrees of reaction. The relative amounts of the several products reflect their ease of formation. As a result of their receptivity, the synthesis of many different derivatives is possible.

OXIDATION

Glycerol can theoretically yield eleven oxidation products containing the original three-carbon chain. All of these compounds have been isolated and identified, but in some cases they are prepared by indirect methods rather than by direct oxidation of glycerol.



Glycerol is stable to atmospheric oxygen under ordinary conditions but is readily oxidized by some other oxidants. The stronger oxidants carry the reaction to completion, forming CO_2 and water. These reactions are the basis of several methods for the quantitative determination of glycerol[1]. Partial oxidation is generally difficult to control to give a large yield of a single product.

Oxidation with Dichromate and Permanganate

Oxidants such as potassium permanganate, potassium or sodium dichromate and chromic acid oxidize glycerol smoothly to CO_2 and H_2 in strongly acid solution. In neutral solution they form glyceraldehyde and dihydroxy acetone as the principal products. As the oxidizing solution is made more alkaline, increasing amounts of glyceric acid ($C_3H_6O_4$) are formed[2]. Using initial concentrations of 0.03M glycerol and potassium permanganate, Tronov[3] found the average value of k, the velocity constant for oxidation, to be 9.46×10^{-4} in neutral solution at 21° C.

Glycerol and potassium permanganate crystals react violently and may even ignite.

Oxidation with Periodic Acid

Periodic acid is a selective oxidizing agent which reacts with compounds with vicinal hydroxyl groups, breaking the bond between the adjacent carbinol groups and leaving them as aldehydes and ketones. With glycerol the carbon chain is broken on each side of the central carbon. The two end carbons produce formaldehyde and the central one gives formic acid, the reaction being quantitative[4]. The rate of this reaction is somewhat affected by pH, being more rapid in the neutral range than the acid range[5].

Oxidation with Lead Tetraacetate

Lead tetraacetate, like periodic acid, will oxidize polyhydric alcohols with adjacent hydroxyl groups. Two moles of formaldehyde and one mole of formic acid are formed from one mole of glycerol[6]. The reaction is not quantitative because of a secondary reaction in which the formic acid is oxidized[7].

Oxidation with Hydrogen Peroxide

When glycerol is distilled with hydrogen peroxide which is added intermittently, it is quantitatively converted into formic acid while glyceric and glycolic acids are formed as intermediate products[8]. Glycerol oxidized by hydrogen peroxide in a strongly alkaline solution results in the formation of formaldehyde and the production of hydrogen, but neither is formed when the oxidation takes place in a less alkaline medium.

Glycerol oxidized by hydrogen peroxide in the presence of various salts produces several products including glyceraldehyde. A number of workers have studied this process as a means of producing glyceraldehyde in quantity[9].

Oxidation with Bromine

Dihydroxyacetone results from the oxidation of glycerol with bromine and sodium carbonate[10] and by the oxidation of lead glyceroxide with bromine vapors[11].

Oxidation Catalyzed by Radiation

Exposure of an aqueous solution of glycerol (2.752 moles per liter) to the radiation from a preparation containing 0.11 gm. of radium for one year resulted in the production of some acetic acid and a lesser amount of formic acid[12].

Oxidation with Salts

Glycerol is oxidized by heating with certain salts such as mercuric chloride, potassium mercuric iodide or any copper salt[13].

Oxidation with Free Oxygen

In the presence of catalysts, glycerol may be oxidized with atmospheric oxygen. When kept in contact with iron or copper it becomes acid and corrosive to the metals. Heat accelerates this action and as the metal goes into solution the catalytic action is intensified. At ordinary temperatures, glycerol reacts with oxygen in the presence of potassium or sodium hydroxide[14], while at body temperature it is readily oxidized in aqueous solution with ferro-pyrophosphate ($Na_8Fe_2(P_2O_7)_3$)[15]. Atmospheric oxidation may also be induced by ferrous hydroxide or sodium sulfite[16].

Decomposition when Heated with Caustic

Glycerol, heated with solid or fused caustic, is decomposed with the formation of various products which depend on the temperature and amount of caustic. A quantitative study of the action of caustic on glycerol was made by Fry and Schulze[17].

Oxidation by Electrolysis

Glycerol with dilute sulfuric acid electrolyzed between a lead anode and platinum cathode in separate chambers and avoiding heat, gives formaldehyde, formic acid, tartaric acid, trihydroxy glutaric acid, I-arabinose, oxygen, carbon monoxide and carbon dioxide at the anode[18].

Photochemical Oxidation

Glycerol is stable to sunlight for practical purposes, however, prolonged exposure or intense radiation in the presence of air will cause oxidation, particularly if metals such as iron and copper are present. The oxidation is also accelerated by water or hydrogen peroxide in small amounts[19].

The photochemical reaction between glycerine and the ferric ion was followed volumetrically by titrating ferric chloride and glycerine diluted with sulfuric acid and Zimmerman's solution against 0.033N potassium permanganate, $KMnO_4$. The rate of the reaction was found to vary with the light source, thus ultraviolet lamp > daylight > darkness (no reaction). The reaction was inhibited by raising the pH of the solution to 5-6 or by the addition of phosphoric acid[20].

REDUCTION

Catalytic Hydrogenation

Glycerol is easily reduced to propylene glycol (1,2,-dihydroxypropane) with hydrogen at pressures from 10 to 100 atmospheres and temperatures above 150° C. Many catalysts may be used, e.g., Ni, Fe, Pt, Au, Hg, copper chromite or tungstic acid[21].

Reduction with Hydriodic Acid

Glycerol heated to 135° to 140° C with an excess of hydriodic acid is reduced to isopropyl iodide. This reaction is the basis of the Zeisel-Fanto analytical method for determining glycerol (1, pg. 216).

ESTERS

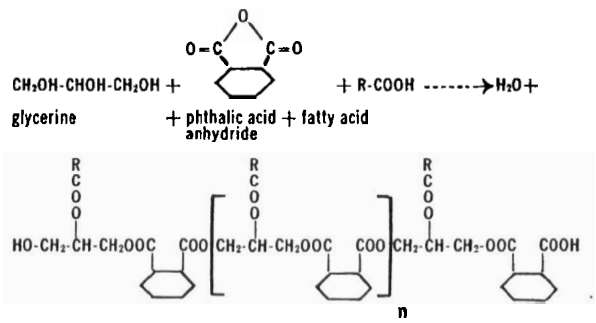
Esters of Organic Acids

The esters of glycerol are the commonest and most diverse group of glycerol derivatives. As the natural glycerides, the fats and oils, they occur throughout the animal and vegetable kingdoms. Many glycerides are prepared commercially from glycerol and fatty acids. In addition there are also the esters of inorganic acids.

Since glycerol has three hydroxyl groups and any or all may be esterfied with almost any combination of acid radicals, the number of possible esters is enormous.

Among the most widely used commercial esters are alkyd resins, ester gums, nitroglycerine and monoglycerides. Esters can be prepared by reacting glycerine with an acid, ester, acid chloride, anhydride or by indirect means.

The preparation of alkyds from glycerol and a dibasic acid such as phthalic anhydride illustrates the versatility inherent in the glycerol molecule. In practice, a monobasic acid is added to the reaction to modify the product by blocking some of glycerol's hydroxyls. This results in a soluble resin rather than an infusible crosslinked mass which would be produced if all the hydroxyls reacted with the phthalic acid. The following is a simplified illustration of the reaction with a 1:1:1 mol. ratio of reactants:



By varying the amounts and kind of modifying mono acid, the resin chemist can develop a product to suit a virtually limitless range of coating requirements. The glycerol can also be reacted with a number of polybasic acids rather than the commonly used phthalic acid to produce resins with specific properties for particular applications.

There are five general reactions for the preparation of glycerol esters:

$$C_3H_5(OH)_3 + RCOOH \rightleftharpoons C_3H_5(OH)_2OOCR + H_2O \quad (1)$$
glycerol + acid (esterification)

$$C_3H_5(OH)_3 + RCOOR' \rightleftharpoons C_3H_5(OH)_2OOCR + R'OH \quad (2)$$
glycerol + ester (alcoholysis)

$$C_3H_5(OH)_2OOCR'' + RCOOR' \rightleftharpoons C_3H_5(OH)_2OOCR + R''COOR' \quad (3)$$
glyceride + ester (transesterification)

$$C_3H_5(OH)_2Cl + RCOOM \rightarrow C_3H_5(OH)_2OOCR + M\,Cl \quad (4)$$
$$C_3H_5(OH)_2SO_4M + RCOOM \rightarrow C_3H_5(OH)_2OOCR + M_2SO_4$$
glycerol halohydrin or sulfate plus a metallic salt or soap

$$C_3H_5(OH)_3 + RCOCl \rightarrow C_3H_5(OH)_2OOCR + HCl \quad (5)$$
glycerol + acid chloride (or acid anhydride)

Although monoglycerides are indicated in the above equations, the reactions are also applicable to di-, and triglycerides. They are also subject to catalytic influence. Moreover, the glycerine can be reacted with a number of polybasic acids for particular applications.

The first three equations represent equilibrium reactions, which can be forced to actual completion if one of the products can be removed.

In the esterfication of glycerol, the primary or alpha hydroxyls usually react more readily than the secondary or beta hydroxyl, resulting in a predominance of alpha isomers except in the case of formic acid esters[22]. The proportion of alpha and beta isomers in any ester is established by an equilibrium reaction, made possible by the migration of the acyl groups. This migration is catalyzed by acid, the aliphatic acyl groups migrating more readily than the aromatic[23].

Glycerol Formates

Alpha-glycerol formate may be prepared from alpha-monochlorhydrin and sodium formate, but is unstable and decomposes at 150° C. during vacuum distilation[24]. When glycerol is directly esterified with formic

acid, the beta-hydroxyl reacts more easily than the other two and the reaction product contains principally beta-glycerol monoformate, and alpha, beta glycerol diformate. Glycerol triformate is prepared by repeatedly heating glycerol diformate with concentrated formic acid until a product containing a large proportion of triformate is formed.

Glycerol formates may also be prepared by reaction between carbon monoxide and glycerol at 60-150° C., and 10-100 atm. with an alkaline catalyst[25] and the mono-, and diformates are formed by heating glycerol with oxalic acid.

Glycerol Oxalates

One mole of oxalic acid and 20 moles of glycerol give a mixture of the normal and the acid esters after standing for three months at room temperature. On heating, the normal ester gives acrolein and the acid ester monoformin[26]. Glycerol also reacts with methyl oxalate to produce glycerol oxalate, which decomposes at 220-225° C. to form allyl alcohol, carbon monoxide, carbon dioxide and an oil[27].

Glycerol Acetates

The acetins (mono-, di-, and triacetate esters of glycerol) are the commonest of the short chain fatty acid esters of glycerol and are used principally as solvents and plasticizers.

Glycerol and glacial acetic acid heated together form a mixture of mono-, di-, and triacetins, their proportions depending on the relative amounts of the reactants. Schuette and Sah[28] claim the choice of catalyst plays an important role in directing the reaction to one product or another. Glycerol can also be acetylated by reacting with ketene in the presence of a strong acid[29].

Triacetin can be produced quantitatively by refluxing glycerol with acetic anhydride and a small amount of sodium acetate, or by heating with glacial acetic acid and a catalyst – though the latter is not quantitative it is more economical[30].

The esterification of glycerol with chloracetic acid is a series of bimolecular reactions. The formation of the mono-ester is slower than that of the di-ester, and the formation of the tri-ester is more rapid than either of the preceding steps[31].

Glycerol Propionates

Monopropionin has been prepared from equimolar amounts of glycerol and propionic acid using phosphoric acid as the catalyst[32, 33]. Tripropionin has also been prepared.

Glycerol Butyrates, Valerates and Caproates

Mono-n-butyrin[33], mono-isobutyrin[32], tributyrin and tri-isovalerin[35], mono-n-valerin, mono-isovalerin and mono-n-caproin[32] have been prepared.

Glycerol Esters of Higher Fatty Acids: The Glycerides

The glycerides of the higher fatty acids are universally found in all living matter, both animal and vegetable. They are a basic type of food and of great importance in industry.

The natural fats are triglycerides, with minor amounts of other substances, and with few exceptions are straight chain compounds with an even number of carbon atoms. The acids may be saturated or unsaturated and a few are hydroxylated. The possible number of glycerides that can be formed is very great and the number that has been described is large.

Glycerol Esters of Hydroxy Acids

Glycerol monoglycolate can be prepared by the alcoholysis of methyl glycolate with glycerol[36] and the monolactate made by heating approximately molar amounts of glycerol and a lactic acid ester[37]. Glycerol dilactate may be made by reaction between a glycerol dihalohydrin and an alkali or alkaline earth salt of lactic acid[38].

Glycerol Carbonates

These esters may be prepared by heating such esters as ethyl or phenyl carbonate with glycerol, or reacting glycerol with phosgene in the presence of organic bases such as pyridine, triethylamine or quinoline[39].

Glycerol Esters of Amino Acids

The monoglycerides of amino acids have been prepared in small yields by intimately mixing the sodium salt of the acid with alpha monochlorohydrin under anhydrous conditions. The mono-di-leucine glycerol ester was obtained[40]. Other amino glycerides were studied by Aberhalden[41].

Glycerol Benzoates

Glycerol alpha monochlorohydrin, heated with sodium benzoate for 2 hours at 175° C. produces principally glycerol alpha-gamma dibenzoate. The alpha-gamma dibenzoate is probably formed by ester interchange between two molecules of the monobenzoate.

Glycerol alpha-monobenzoate is a viscous, water-soluble liquid which decomposes when distilled. Glycerol alpha-gamma dibenzoate is a viscous hygroscopic oil which is only slightly soluble in water. Glycerol dibenzoate mixed with a lesser amount of glycerol monobenzoate is also formed when an equimolar mixture of benzoic acid and glycerol is heated at 225° C. for ten hours in an atmosphere of CO_2[42].

Glycerol tribenzoate may be prepared from glycerine and benzoyl chloride by the Schotten-Baumann reaction. It occurs in two forms, one commonly melting at about 72° C. the other at 76° C.[42]. If the higher melting form

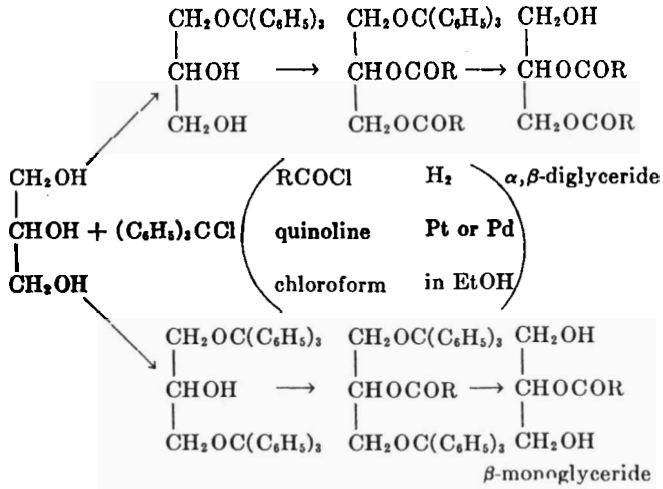
is recrystallized from ligroin or is fused and allowed to cool slowly the low melting form is obtained.

Monosodium glyceroxide and para-nitrobenzoyl chloride give glycerol alpha (para-nitrobenzoate)[43]. The preparation of glycerol tribenzoate and glycerol tris (3,5-dinitrobenzoate) can be used for the identification of glycerol (1, pg. 174).

PREPARATION OF GLYCERIDES OF KNOWN STRUCTURE

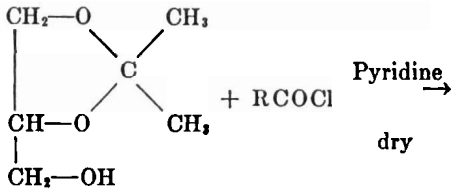
The preparation of glycerides of known structure is important in the study of glycerides themselves and as a step in establishing the structure of many other glycerol derivatives. This proof is made difficult by the ease with which the ester groups migrate. Migration is catalyzed by acid, but alkali and increased temperatures also accelerate it. There is a greater tendency for groups to move from the beta to the alpha position than to move in the opposite direction.

Glycerides can be prepared without migration of the ester group by the use of glycerol trityl ethers as intermediate compounds. One or two hydroxyls of the glycerol are blocked by etherification with the trityl group. The remaining hydroxyls are then esterfied with an acid chloride after which the trityl groups are removed by catalytic hydrogenation with Pt black in absolute ethyl alcohol at 40-50° C. and 45 pounds pressure psi. Due to mildness of the conditions the ester group does not shift.

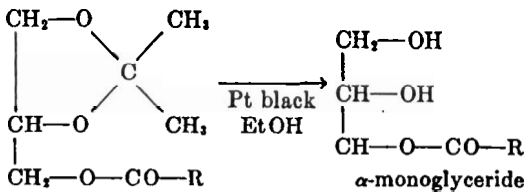


Trityl chloride reacts with both the secondary and the primary hydroxyl groups and therefore the structure of the trityl ethers must be established in every case[44, 45].

A method for preparing monoglycerides of known structure makes use of the glycerol acetals and ketals. Benzylidene glycerol and isopropylidene glycerol are frequently used in this reaction. The former compound exists in isomeric forms. In one the alpha and beta hydroxyls are blocked, in the other the gamma and alpha hydroxyls. Isopropylidene glycerol is obtained only as the alpha, beta-isomer by the usual method of synthesis. By acetylating the proper isomer and removing the acetal or ketal group by catalytic hydrogenation or mild hydrolysis, a glyceride of known structure is obtained[46]. Special care must be taken to avoid migration.



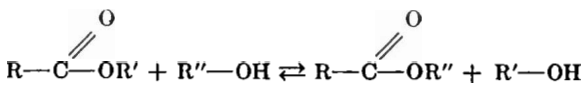
α,β-isopropylidine glycerol



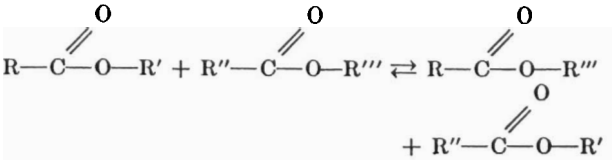
α-monoglyceride

PREPARATION OF GLYCERIDES BY ESTER INTERCHANGE

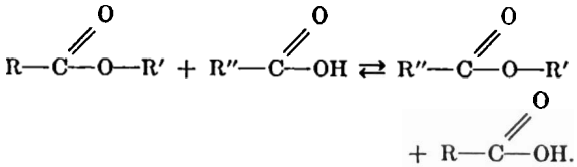
Ester interchange can take place in three ways: (1) by the transfer of an acid radical from an ester to an alcohol. This is known as alcoholysis,



(2) By the exchange of acid radicals between two esters,



(3) By the replacement of an acid radical in an ester with the radical of a free acid.



Only the first two methods are used in the commercial preparation of glycerides.

A variety of catalysts may be used to promote the first two reactions but soaps and alkali are the most commonly used. Temperatures of 200°-250° C. are effective and reduced pressure in an inert atmosphere

may be used if necessary[47]. A number of different catalysts under varying conditions have been suggested[48].

The preparation of mono-, di-, and triglycerides of the fatty acids by these various methods is of great economic importance. The mono-, and diglycerides are surface active and emulsifying agents with extensive commercial use. The preparation of triglycerides makes possible the rearrangement of fatty acid groups to produce oil of greater value than the original. The synthetic glycerides may be prepared by direct esterification of the fatty acid with glycerol or by alcoholysis of a fat with glycerine to obtain mono-, or diglycerides. Time, temperature and catalysts for the reaction vary and the subject has been extensively reviewed[49, 50]. A method has been devised by Brandner and Birkmeier for determining the relative esterifiability of the primary and secondary hydroxyl groups of glycerol[51]. Contrary to a theory previously advanced[52], the primary and secondary hydroxyls are not equally esterifiable. The equilibrium constant favoring esterification of primary hydroxyl over secondary is ca 2.3 at reaction temperature (200° C.) and between 6 and 10 at room temperature. Since the equilibrium constant is substantially different at room temperature from that at reaction temperature, monoglycerides as customarily prepared are not at equilibrium at room temperature and undergo intramolecular migration of acyl groups from beta to alpha hydroxyl positions. In another recent work[53] fatty acids, i.e., lauric, stearic, oleic, etc., were reacted with glycerine under controlled conditions. Beta monoglycerides constitute a considerable proportion at various stages of the reaction, particularly below 180°. Above this temperature there is a tendency to migrate to the alpha position. These same workers pointed out that the reactivity of fatty acids is greater with low molecular weight and unsaturated fatty acids. More recent studies[54] on the 3 dimensional esterification of a polybasic acid and a polyhydric alcohol, show that esterification depends only on the number of functional groups and the initial molar ratio of the carboxyl and hydroxyl groups and is independent of the temperature, catalyst and solvent.

ESTERS OF INORGANIC ACIDS

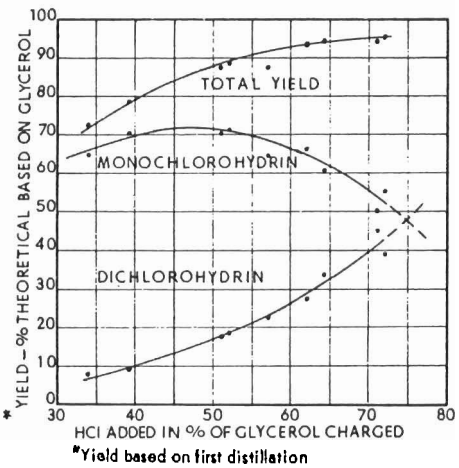
Halohydrins

The glycerol esters of the hydrogen halides are known as glycerol halohydrins i.e., chloro-, bromo-, and iodohydrins. In any preparation of the halohydrins from glycerol and the corresponding acid, a mixture of mono- and di-halohydrins is obtained, the predominance of one or the other being determined by the conditions of the reaction. Both alpha and beta isomers are formed.

The principal use of the halohydrins is in synthesis, as the halogen atoms offer a good means of substituting other groups in the glycerol molecule.

Chlorohydrins

Glycerol monochlorohydrin is a heavy, slightly viscous and colorless liquid with a sharp, slightly sweet odor, soluble in water, alcohol, glycerol, ether and acetone[55]. It is prepared from glycerol and hydrogen chloride gas with acetic acid as the catalyst. The amount of hydrogen chloride used determines the yield of both mono-, and dichlorohydrin, Fig. 1[56].



*Yield based on first distillation

The product obtained by this method is mainly the alpha isomer, the beta isomer being formed to the extent of 10-15 percent[57].

The monochlorohydrin may also be prepared from glycerol and aqueous hydrochloric acid[58] and pure alpha monochlorohydrin by hydrolyzing epichlorohydrin with an acid catalyst such as sulfuric acid[59]. Beta monochlorohydrin may be prepared by the action of hydrogen chloride on glycidol.

The alpha and beta isomers are separable due to their difference in reaction rates with acetone.

Many different conditions of temperature, concentration and catalyst have been tried in the preparation of glycerol chlorohydrin. The literature to 1931 has been reviewed by Gibson[60].

Among other routes, glycerol monochlorohydrin can be made by the addition of hypochlorous acid to allyl alcohol[55], a step that may be used in the preparation of glycerol from propylene.

Glycerol dichlorohydrin is a heavy, mobile and colorless liquid with a rather sweet odor. It may be prepared by the action of hydrogen chloride gas on glycerol, resulting in both the alpha-gamma, and the alpha-beta isomers. Catalysts accelerate the action, glacial acetic acid being the most commonly used. This process is similar to that for the preparation of monochlorohydrin except the hydrogen chloride is added to saturation. An excess of HCl gas, 2% acetic acid and a temperature of 100-110° C. are recommended[61, 62]. Pure glycerol

alpha, gamma-dichlorohydrin is prepared by converting ordinary dichlorohydrin (mixtures of both isomers) to epichlorohydrin and hydrolyzing these with hydrochloric acid. Several techniques for the improvement of chlorohydrin manufactured by the use of solvents have been patented[63].

Glycerol trichlorohydrin (1,2,3-trichlorpropane) is a heavy, mobile colorless liquid that can be hydrolyzed to glycerol, and may be prepared by the action of thionyl chloride on dichlorohydrin[61]. However it is more easily prepared by chlorination of propane or propylene and is usually considered a derivative of them rather than of glycerol. This chlorination of propylene is a basic step in the preparation of synthetic glycerine by the Shell Chemical Company method. Since the halogen atoms offer a good means of substituting other groups in the glycerine molecule, they are useful in synthesis. Some too find applications as solvents.

Bromohydrins

Glycerol monobromohydrin is a colorless, heavy, moderately viscous liquid, and occurs in alpha and beta isomeric forms. It may be prepared directly from glycerol by the action of hydrobromic acid, or dry hydrogen bromide[65, 66]. It can also be formed from allyl alcohol and bromine water[55] or by electrolyzing sodium bromide in the presence of allyl alcohol[67].

Glycerol dibromohydrin is a heavy, colorless liquid which has two isomers, the alpha, gamma and the alpha, beta forms. Both are produced by the action of hydrobromic acid, or the action of liquid bromine and red phosphorus on glycerol[68].

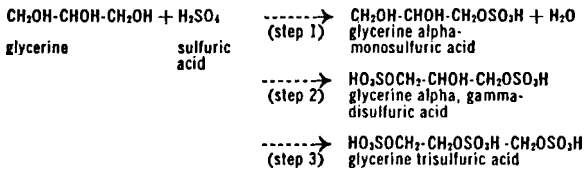
The tribromohydrin has been prepared from glycerol but is more commonly prepared, like the trichlorhydrin, from hydrocarbon sources.

Iodohydrins

The glycerol iodohydrins are not prepared directly from glycerol and hydriodic acid, but from the chlorohydrins, by replacing the chlorine with iodine[69].

SULFURIC ESTERS

Glycerol sulfuric esters are easily prepared by the direct reaction of glycerol with sulfuric acid. The complete esterification of glycerol with sulfuric acid can be represented by three steps:



Four factors influence the course of this reaction: time, temperature, molar ratio of glycerol to acid, and the concentration of the acid. The degree of esterification of the glycerol depends not only on the amount of acid but its concentration.

The salts of glycerol sulfuric acids may be prepared by neutralization and these in turn can be used for the preparation of esters, ethers and amines by double decomposition reactions.

Glycerol Nitrite

The trinitrite of glycerol $CH_2(\text{-O-NO})\text{-}CH(\text{O-NO})\text{-}CH_2(\text{O-NO})$ has been obtained by passing dry nitrous acid anhydride N_2O_3 into cooled glycerine[70].

Glycerol Nitrates

Glycerol mononitrate is a viscous, hygroscopic liquid, soluble in water, alcohol and ether. It can occur either as the alpha or beta isomer depending on the conditions of preparation. In crystalline form they detonate easily but the liquid form is insensitive to shock[71], thus they are not sufficiently powerful to be of value as explosives. The mononitrate may also be prepared by the action of dilute nitric acid on glycidol or the nitration of glycerol. By this latter method the di- and tri-nitrates are also formed[72].

Glycerol dinitrate is a colorless, odorless oil, more viscous and volatile than the trinitrate. There are two isomeric forms, alpha, gamma and alpha, beta; both are non crystallizable. The dinitrate is similar to the trinitrate in explosive qualities, when exploded it decomposes according to the following equation.

$$C_3H_6N_2O_7 \rightarrow 2CO_2 + CO + 2H_2O + N_2 + H_2$$

Glycerol trinitrate, commonly called nitroglycerine, was discovered in 1846. It is a vasodilator and hence is used medically in the treatment of angina pectoris and asthma. Its use as an explosive was developed by Alfred Nobel when in 1867 he discovered it could be absorbed on diatomaceous earth to form an explosive much easier to handle than liquid nitroglycerine.

Glycerol trinitrate is a colorless to pale yellow oil, practically odorless at ordinary temperatures, but with a faint characteristic odor at 50° C., It is volatile with steam and when heated it starts to decompose at 50-60° C. Decomposition increases with rising temperatures and about 145° C. it bubbles vigorously. At 281° C. it explodes.

There are two crystalline forms of the trinitrate; the stable form, dipyramidal rhombic crystals, M.P. 13.2-13.5° C., and the labile form, glassy appearing triclinic crystals, M.P. 1.9-2.2° C. It supercools easily.

Glycerol trinitrate in small amounts can be ignited and burned without explosion. The temperature required to cause an explosion will vary with conditions, 200-250° C. is the temperature attained with the usual methods of testing.

The trinitrate may be formed by nitration of glycerine with HNO_3, i.e.,

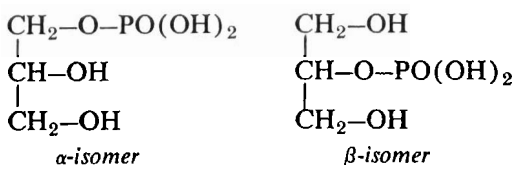
$$C_3H_5(OH)_3 + 3\ HNO_3 \rightleftarrows C_3H_5(ONO_2)_3 + 3H_2O$$

Actually the reaction is reversible and without the addition of a strong dehydrating agent a large excess of nitric acid is needed. Commercially sulfuric acid is used as the dehydrating agent. The reaction is exothermic and the temperature of the mixture must be kept between 12 and 25° C.

Diglycerol tetranitrate is formed by the nitration of diglycerol with mixed acid (40% nitric — 59.5% sulfuric). It is viscous, non-hygroscopic, insoluble in water, soluble in alcohol and ether, is explosive and is sometimes added to glycerol trinitrate to produce a low freezing mixture. Dinitrochlorohydrin and various dinitrates are also used in making non-freezing dynamites.

Glycerol Phosphoric Acid Esters

Glycerine will form esters with phosphorous[70] and phosphoric acid. There are a large number of theoretically possible esters with phosphoric acid as a result of each molecule having three functional groups. The most commonly used phosphoric acid esters are the simplest:



This, and more particularly its salts of ammonium, calcium, iron, potassium and sodium, are used in pharmaceutical preparations and soft drinks. Esters of glycerol phosphoric acid occur widely in nature, especially in lecithin, and the products of animal carbohydrate metabolism. For a review of the literature and a discussion of the structure and solubility of the salts of glycerol phosphoric acid see DuBois, Inc. & Eng. Chem. *6*, 122-128 (1914).

Esterification of glycerol with phosphoric acid at 100° C. under normal pressure produces mainly the alpha isomer. If the glycerol is esterified by heating with sodium dihydrogen phosphate the beta isomer is the principal product. The two isomers are interconvertible in acid solution but stable in the presence of alkali.

The proportion of alpha and beta isomers can be estimated by treatment with periodic acid. This will quantitively oxidize the alpha isomer and not affect the beta.[74]

Esters other than glycerol monophosphoric acid can be prepared by suitable changes in the temperature and concentration of the reactants. Glycerol phosphoric acids may also be prepared by the reaction of chlorohydrins with di-, or trisodium phosphate, glycerol with disodium phosphate, epichlorohydrin with phosphoric acid or mono- or disodium phosphate, glycerol with phosphorus oxychloride, and by the oxidation of allyl esters of phosphoric acid.

Glycerol Esters of Arsenious Acid

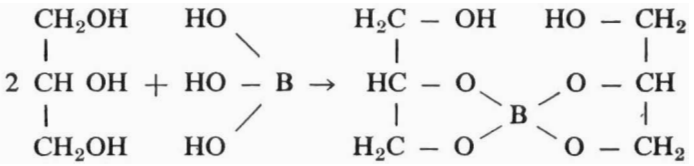
The arsenious ester of glycerol $C_3H_5AsO_3$ is prepared by heating glycerol and arsenic trioxide with stirring. Water is removed by azeotropic distillation with benzene, toluene or xylene[75].

Glycerol Esters of Boric Acid

Glycerol with boric acid titrates as a monobasic acid and has been used for years to titrate with phenolphthalein against an alkali. The glycerol is added to the boric acid as an activator.

Glycerol and boric acid heated together to expel water form a triester, though the exact nature of the complex has not been definitely established.

It may be represented as follows:[76]



$$H_3O + 2H_2O \quad \text{or} \quad H^+ + 3H_2O$$

Borax ($Na_2B_4O_7.10H_2O$) added to glycerol in water solution becomes acid. The borax dissociates and the same glycerol-boric acid compound is formed that is obtained with boric acid[72].

ETHERS

Glycerol can form mono-, di-, and triethers. They may be either ethers of glycerol with itself (polyglycerols), inner ether (glycidol), or mixed ethers of glycerol with other alcohols.

Polyglycerols

For the commercial production of polyglycerols, glycerol is heated with an alkaline catalyst at elevated temperatures (200° C.-275° C.) at normal or reduced pressure. A stream of inert gas may be used to blanket the reaction and help remove the water of reaction. There are many patents and disclosures covering variations of these factors, but the essentials remain the same. How well the process steps are applied and utilized appears to make the difference in the quality of the products produced. Light color, good odor, and flavor are essential for the many edible and industrial applications that are contemplated. The polyglycerols are similar to glycerine but offer greater flexibility and functionality. In the homologous series of polyglycerols, their molecular weight and the number of hydroxyls can increase thus providing versatile polyols which can offer

advantages per se or through the derivatives that may be synthesized.

In the series of polyglycerols which are produced by this method some unchanged glycerine will remain in the mixture. The resulting products are mixtures of a range of molecular weights but averaging out to a mean molecular weight of diglycerol, triglycerol, etc. The application of vacuum (stripping) to remove the free glycerine is helpful in narrowing the range of molecular weights in the resulting product. The hydroxyl value, viscosity, refractive index, and the amount of water removed in the reaction are used as controls in the production of consistent products.

In the formation of polyglycerols, an ether linkage for every 3 carbon atoms results with the splitting off of water. This unit is repeated as the polymer chain increases.

Table I gives some physical constants and the theoretical hydroxyl numbers for products having the indicated average composition.

TABLE I. SOME PHYSICAL AND CHEMICAL CHARACTERISTICS OF POLYGLYCEROLS

Compound	Molecular Weight	Number of OH Groups	Calculated OH Value	Found OH Value	Viscosities CTKS @ 150°F	Viscosities CTKS @ 180°F
Glycerol	92	3	1830	1828	45	25
Di-glycerol	166	4	1352	1320	287	110
Tri-glycerol	240	5	1169	1166	647	230
Tetra-glycerol	314	6	1071	1082	1067	340
Penta-glycerol	388	7	1012	1028	1408	430
Hexa-glycerol	462	8	970	1010	1671	548
Hepta-glycerol	536	9	941	972	2053	620
Octa-glycerol	610	10	920	951	2292	715
Nona-glycerol	684	11	903	903	2817	858
Deca-glycerol	758	12	880	888	3199	954
Penta deca-glycerol	1128	17	846	854	4893	1192
Triaconta-glycerol	2238	32	803	818	6206	1716

Polyglycerols ranging from diglycerol to triacontaglycerol have been prepared. The polyglycerols range from viscous liquids to solids. They are soluble in water, alcohol, and other polar solvents. They act as humectants much like glycerine but have progressively higher molecular weights and boiling points. The polyglycerols as a homologous series of polyols are valuable intermediates. Table I lists the polyglycerol types available for esterification and their molecular weight range. Products which are based on polyglycerols are useful as surface active agents, emulsifiers, plasticizers, adhesives, lubricants, and other compounds which are utilized in both edible and industrial applications.

Polyglycerols and polyglycerol esters are utilized by the body and broken down to glycerine and fatty acids. Food and Drug approval for polyglycerol esters up to the decaglycerol esters has been granted in the United States, and across the board clearance has been given to such compounds in Great Britain. Compounds varying from water to oil solubility can be produced from polyglycerols depending on the type and amount of the fatty acids used. Hydrophilic to lipophilic properties can be built into the structure by varying the number of free hydroxyls.

Polyglycerol Esters

Polyglycerol esters have been prepared from the various polyglycerols available. Partial and complete esters of saturated and unsaturated fatty acids form a variety of derivatives of polyglycerols ranging from diglycerol (2 moles) to triacontaglycerol (30 moles).

Partial esters of polyglycerols may be prepared by (a) direct esterification and (b) transesterification reactions. The variations in molar ratios of the fatty acid or the oil will determine the formation of mono-, di-, or polyester from the respective polyglycerol.

Completely esterified products may be prepared from a given polyglycerol by using excess amounts of the fatty acids in the esterification reaction.

Table III, (a), (b) and (c), gives some constants of typical polyglycerol esters which are in commercial production and being used in foods, pharmaceuticals, cosmetic preparations, and other industrial applications.

Table IV, (a), (b) and (c), gives some constants of typical polyglycerols which have been completely esterified. In essence such products are polymer oils and serve as high molecular weight functional fluids and solids.

Derivatives of polyglycerols are not limited to their fatty acid esters. Reaction products of hydroxy acids, ethylene oxide, propylene oxide, isocyanates, etc. have been reported. These products show apparent application in foods, pharmaceuticals, and cosmetic preparations.

The polyglycerols and polyglycerol esters are now available in such quality and variety that it is quite possible that their application and use will show considerable growth in the next few years. It is one of the potential outlets for glycerine and glycerine derivatives that has been a sleeping giant coming to life. An indication of the areas of application is illustrated in Table II.

TABLE II. AREAS OF INDICATED APPLICATION

POLYGLYCEROLS . . . . . POLYGLYCEROL ESTERS

LUBRICANTS	URETHANE INTERMEDIATES	FUNCTIONAL FLUIDS
PLASTICIZERS	ADHESIVES	SURFACE ACTIVE AGENTS
PAINT & VARNISH VEHICLES	CROSS LINKING AGENTS	DISPERSANTS
GELLING AGENTS	HUMACTANTS	EMULSIFIERS
	TEXTILE FIBER FINISHES	

TABLE III(a). SOME PHYSICAL AND CHEMICAL CHARACTERISTICS OF POLYGLYCEROL ESTERS

Chemical Identity	Color Gardner	Hydroxyl Value	Sap. No.	Iod. Val.	FFA	Form	Spec. Grav.	Melting Point
Decaglycerol Monolaurate	9+	690	58.7	2.3	1.0	Viscous liquid	1.15	Below zero
Decaglycerol Monomyristate	11+	577	70.3	2.5	0.8	Semisolid	1.11	13.8
Decaglycerol Monopalmitate	10+	583	63.7	2.5	0.9	Semisolid	1.05	37.5
Decaglycerol Monostearate	13	598.8	70.8	2.4	0.5	Semisolid	1.04	51.9
Decaglycerol Monooleate	11+	567	68.2	27.3	0.7	Viscous liquid	1.13	Below zero
Decaglycerol Tristearate	13+	282.7	121.8	1.7	1.2	Waxy solid	1.03	51.6
Decaglycerol Tetraoleate	7−	246.5	141.3	55.1	3.7	Liquid	1.00	Below zero
Decaglycerol Hexaoleate	10	148.1	153.9	63.8	2.2	Liquid	0.97	Below zero
Decaglycerol Octaoleate	6	83.2	168.0	68.9	5.7	Liquid	0.95	Below zero
Decaglycerol Decastearate	5+	47.8	169.8	2.0	8.1	Waxy solid	0.92	53.4
Decaglycerol Decaoleate	6	32.3	177.9	70.6	5.8	Liquid	0.94	Below zero
Decaglycerol Decalinoleate	7	26.8	148.7	123.6	4.9	Liquid	0.94	Below zero
Hexaglycerol Monostearate	12	431	78.0	3.0	2.0	Waxy solid	0.99	52.2
Hexaglycerol Monooleate	8−	481	82.0	33.0	5.0	Viscous liquid	1.07	Below zero
Hexaglycerol Dioleate	9	343	130.0	51.0	1.6	Liquid	1.01	Below zero
Hexaglycerol Hexaoleate	5−	65	177.1	71.7	4.7	Liquid	0.93	Below zero
Triglycerol Monostearate	8	325	125.1	2.5	4.1	Waxy solid	1.03	52.5

TABLE III(b). EXAMPLES OF PARTIAL ESTERS PREPARED BY TRANSESTERIFICATION

	A No.	Sap. No.	OH No.	pH (3% sol)	% mono Glyceride	% free Glycerine	IV
3-Mono cottonseed oil ..	6.2	133.1	308.4	5.1	21.3	3.0	74.6
3-Mono palm oil	5.4	132.2	—	5.0	26.3	2.8	38.9
3-Mono shortening oil ..	4.8	130.1	327.8	6.1	21.7	3.2	41.3
5-Di tallow oil	—	163.0	—	6.8	18.5	2.2	—
5-Di shortening oil	1.8	121.9	361.5	—	20.3	3.3	39.6
6-Sesqui palm oil	0.6	106.5	369.7	7.7	—	—	28.3
6-Di shortening oil	4.4	128.3	303.3	6.1	14.4	2.0	47.4
6-Di cottonseed oil	7.0	126.5	—	5.3	17.6	3.0	73.4
6-Di peanut oil	4.8	123.8	297.5	5.7	12.5	1.8	58.8
9-Tri peanut oil	5.6	120.0	299.1	5.2	10.9	1.7	58.6
9-Tri shortening oil ...	6.0	122.4	296.8	5.9	10.8	1.7	46.6
10-Mono corn oil	7.4	88.8	—	4.7	11.8	4.9	52.4
10-Di shortening oil ...	0.4	92.7	364.7	6.4	7.3	—	—
10-Di palm oil	2.0	83.9	413.1	—	8.2	—	—
10-Tri peanut oil	7.6	121.6	305.5	4.6	11.6	1.9	54.6
10-Tri cottonseed oil ...	7.2	117.3	—	6.1	14.3	3.4	64.3
10-Tri shortening oil ..	6.6	121.4	293.1	5.3	10.1	1.5	44.2
10-Tetra cottonseed oil .	5.2	128.2	262.0	6.0	—	—	—
10-Penta cottonseed oil .	6.4	136.2	237.3	5.9	—	—	—
10-Penta shortening oil .	5.6	138.5	104.1	6.1	—	—	—
30-Deca peanut oil	6.8	120.6	296.2	5.2	10.2	1.6	55.8

Table III(c). Esters for the Paint, Varnish and Urethane Industry

Chemical Identity	A No.	Sap. No.	Hydroxl Value	Iod. Val.	Visc. @ 168°F CPS	Color Gardner
Triglycerol Monolinoleate	.4	145.0	368.9	105.7	—	5+
Triglycerol Pentalinoleate	5.0	180.4	46.0	130.8	—	—
Triglycerol Monolinolinate	.4	111.0	334.9	102.8	322	11
Triglycerol .5 linoleate	2.4	129.5	393.5	90.8	106	7
Triglycerol Trilinoleate	2.6	169.1	119.1	117.3	30.1	6
Triglycerol Tetraricinoleate	3.2	172.5	175	87.2	86.6	11+
Triglycerol .75 Ricinoleate	1.0	128.0	446.4	84.9	145	7
Triglycerol .5 Ricinoleate	2.2	123.9	480.1	82.1	138	8+
Hexaglycerol .87 linoleate	1.6	104.3	438.1	89.2	331	7
Hexaglycerol 1.7 linoleate	4.8	119.2	59.9	119.6	34.7	3
Hexaglycerol .87 Ricinoleate	1.4	115.5	227.0	88.9	273	6
Hexaglycerol 6.6 Ricinoleate	6.0	171.7	63.1	111.5	96.8	5
Hexaglycerol .6 Ricinoleate	2.6	121.8	420.7	61.9	209	15+
Hexaglycerol .8 Ricinoleate	2.4	103.9	470.5	80.0	1660	6
Decaglycerol .9 Ricinoleate	1.8	85.8	486.9	64.7	3580	7
Decaglycerol .8 Ricinoleate	3.8	53.1	284.2	32.3	4175	10
Decaglycerol Decalinoleate	9.0	168.8	130.3	124	—	7
Decaglycerol Trilinoleate	7.4	—	297.6	81.2	—	7
Decaglycerol Dilinoleate	8.0	98.4	385.5	61.9	1525	12+
Decaglycerol Monoricinoleate	.4	83.4	452	—	—	12+
Triglycerol 1.5 adipate	2.0	—	791.1	—	1530	7-8
Triglycerol 1.7 adipate	1.0	—	850	—	1600	7-8
Triglycerol Monoadipate	1.8	—	661.6	—	2200	10-11

Table IV(a). Triglycerol Simple Esters

Acid	A No.	Sap. No.	Smoke °F	Flash °F	Fire °F	Sp. Gr. 25/15°C	Viscosity CPS. Brookfield Spindle No. 1 59°C 6 RPM	12 RPM	30 RPM	60 RPM
Acetic	.4	644.7	—	405	420	—	15	18.0	21.0	22
Isopentanoic	1.0	428.7	275	485	530	—	6	9.5	10.8	12.4
2-methyl Pentanoic	.12	378.7	290	410	440	1.010	7	10	11.2	12.5
2-ethyl Hexanoic	.90	261.3	305	465	480	0.978	11	13.5	15.2	16.5
Caprylic	.14	324.1	—	475	505	0.977	15	15	16	17
Pelargonic	.15	318.5	365	520	550	0.967	15	15.5	17.2	18.4
iso-octanoic	1.40	147.5	305	480	510	0.982	20	21.5	22.2	23.0
iso-decanoic	1.00	279.1	335	495	540	0.959	22	23	25	26.5
2-ethyl Butyric	.30	312.7	265	445	485	1.009	36	36.5	33.0	30.7

Table IV(b). Hexaglycerol Simple Esters

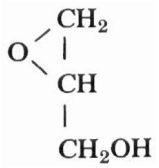
Acid	A No.	Sap. No.	Smoke °F	Flash °F	Fire °F	Sp. Gr. 25/15°C	Viscosity CPS. Brookfield Spindle No. 1 59°C 6 RPM	12 RPM	30 RPM	60 RPM
Acetic	.7	584.1	225	445	465	—	67	72	73	73.6
Isopentanoic	.20	388.6	305	465	485	1.051	17	18.5	21	21.8
2-methyl Pentanoic	1.3	351.6	240	405	430	1.029	19	20	21.2	22.6
Caprylic	.08	311.9	—	510	535	.988	20	20.5	23.0	24.5
2-ethyl Hexanoic	.18	267.2	305	485	500	.988	25	25.5	27	27.7
Pelargonic	1.6	293.9	360	520	550	.983	25	25	26	26.8
2-ethyl Butyric	1.0	318.2	300	460	485	.988	30	32.5	34	35.5
iso-decanoic	.10	267.6	320	510	550	.981	38	40	41	42.4
iso-octanoic	.40	304.1	325	500	525	.999	40	42.5	43.2	44.5

Table IV(c). Decaglycerol Simple Esters

Acid	A No.	Sap. No.	Smoke °F	Flash °F	Fire °F	Sp. Gr. 25/15°C	Viscosity CPS. Brookfield Spindle No. 1 59°C 6 RPM	12 RPM	30 RPM	60 RPM
Acetic	.5	534.6	230	415	445	—	160	162.5	162.5	220
2-methyl Pentanoic	.90	320.4	220	420	430	1.038	27	28	29.8	30.4
Caprylic	.06	305.2	—	510	540	0.997	28	30	32.2	33.6
Pelargonic	1.8	276.3	330	505	555	0.992	35	37	38.2	39.1
2-ethyl Hexanoic	.5	—	325	495	525	0.999	39	40	41.6	42.6
Isopentanoic	.4	285.6	255	440	465	1.070	40	42.5	43	44.5
2-ethyl Butyric	1.2	432.8	285	475	495	1.040	45	48	50	51
iso-octanoic	.4	295	280	495	525	1.005	64	65	67	67.2
iso-decanoic	.4	254.2	365	535	575	0.982	75	73	76	76.6

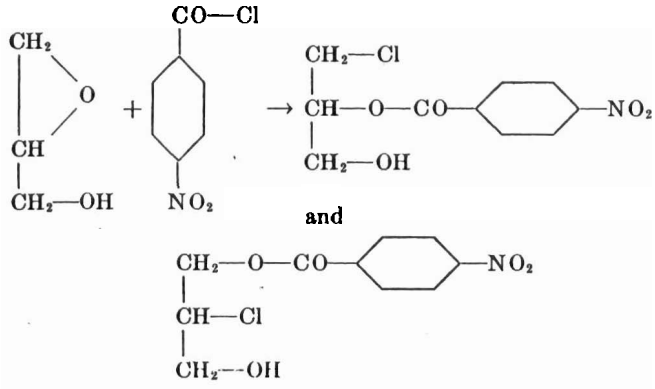
EPOXY COMPOUNDS – GLYCIDOL

Glycidol, 2, 3-epoxy-1-propanol is the inner ether of glycerol and may also be considered as a derivative of ethylene oxide.



The epoxy group is very reactive. Glycidol is a colorless liquid with a slightly sweet odor. It is soluble in ether, alcohol, water, acetone, chloroform and benzene, slightly soluble in petroleum ether and xylene. Acid accelerates the reactivity of the epoxide group, causing the formation of glycerol with water and an alpha glycerol ether with alcohol. The latter reaction is a convenient method for preparing ethers including diglycerol. Glycidol, when slowly added to a secondary alkylamine, reacts to form an alpha-glyceroldialkylamine. With ammonia or a primary amine it also forms glycerol amines but mixtures are obtained as more than one of the amine hydrogens may react.

Glycidol will also react with an acid or with the anion in a salt solution to form an ester or a halohydrin of glycerol[79]. Acid chlorides also add to glycidol and it has been shown that the epoxy ring can open on either side of the oxygen atom. As a result isomeric products are obtained:[80]



An excess of the acid chloride will react with the remaining hydroxyl group.

Glycidol may be prepared by the action of an alkaline reagent upon either alpha or beta glycerol monchlorhydrin.

Although the preparation of glycidol with the aid of sodium and ether gives the best yield, it is not always feasible to use these reagents. Monochlorhydrin and sodium hydroxide may be reacted in water solution at a temperature below 50° C. After 30 minutes the reaction mixture is neutralized, salt filtered out and the product recovered by distillation. A yield of 85.5% of theoretical is claimed[81, 82].

EPICHLOROHYDRIN

Epichlorohydrin $CH_2\text{-}CH\text{-}CH_2Cl$ (2,3 epoxy 1-chloropropane) is a colorless, mobile liquid with an odor somewhat like chloroform. With water it forms a constant boiling mixture which distills at 88° C. and contains 75% of epichlorohydrin. The epoxy group will react in its characteristic ways, some of which have been discussed in the section on glycidol. The reactivity of the chlorine atom is similar to that in monochlorohydrin. Epichlorohydrin may be prepared in a number of ways, all based upon the reaction of an alkaline substance with glycerol dichlorohydrin. A satisfactory and practical method is to mix dichlorohydrin in 5% excess in lime and water. The reaction takes place at ordinary temperatures and the product is distilled from the reaction mixture at reduced pressure[83]. On a commercial scale it is distilled as formed.

Epichlorohydrin resins are used in water proofing of binding materials, as a solvent for natural and synthetic resins, gums, cellulose esters and ethers, paints, varnishes, nail enamels and lacquers and cement for celluloid.

EPIBROMOHYDRIN

Epibromohydrin $CH_2\text{-}CH\text{-}CH_2Br$ is analogous to epichlorohydrin and is formed from glycerol dibromohydrin in a similar manner, although the reaction goes more easily[83].

MIXED ETHERS OF GLYCEROL

Inner ethers and ethers of glycerol with itself (polyglycerols) have been described. The ethers of glycerol with alcohol and phenols are more numerous and varied in their properties. One, two, or three of the glycerol hydroxyls may be etherified. In addition to the structural isomers of the mono- and di-ethers in which only one kind of group is etherified with the glycerol, there are also structural isomers resulting from the difference in arrangements of dissimilar groups that may occur in di- and triethers.

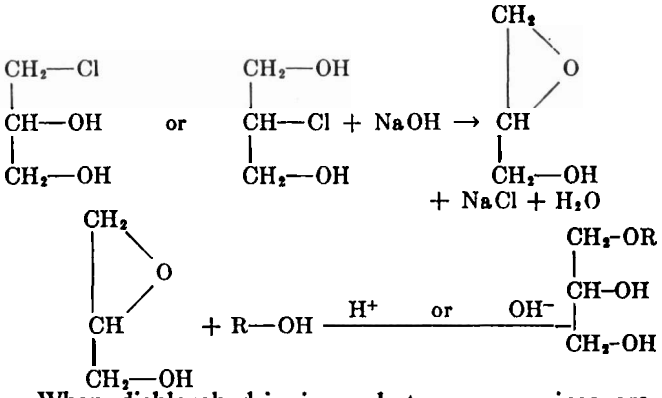
The glycerol ethers are similar to other ethers in that they are chemically stable. Solubility in water is less and solubility in organic solvents greater than glycerol. In partial ethers of glycerol, one or two hydroxyls remain unetherified, the compounds have both alcoholic and ethereal characteristics, the hydroxyls being available for the usual reactions of alcohols. The glycerol ethers have been useful in the proof of structure of glycerol derivatives[84].

Glycerol ethers are important commercially as solvents and plasticizers for cellulose derivatives and lacquers[85], an ingredient of alkyd resins,[86] as chemical intermediates for making detergents and surface active agents,[87] and as perfume fixatives[88].

Glycerol ethers of fatty alcohols occur in natural products. Certain fish liver oils contain ether esters of glycerol which are fatty acid di-esters of alpha-glycerol ethers of fatty alcohols. These ether-esters comprise about 21 per cent of the original oil[89]. They are found less frequently in land animals and in vegetable oils, in lesser amounts. The exception to this is tung oil which contains a considerable amount[90]. The following natural ethers are known: alpha-glycerol octadecyl ether which is called batyl alcohol; alpha-glycerol oleyl ether, called selachyl alcohol; and alpha glycerol cetyl ether which is called chimyl alcohol[91]. Some physical properties of a number of glycerol ethers are given in Table 5. Glycerol ethers are formed by the reaction of glycerol chlorohydrins and an alcohol or phenol in the presence of an alkali. The chlorohydrin first reacts with an alkali to form an epoxy compound which then reacts with the alcohol or phenol to form the ether. The epoxy ring can be formed from either an alpha or a beta chlorohydrin, but when the ring reacts to form an ether, the ether group always goes to the alpha position.

TABLE 5. PHYSICAL PROPERTIES OF SOME GLYCEROL ETHERS

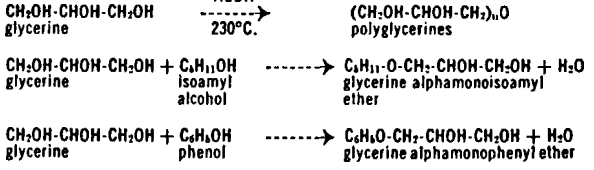
Glycerol Ether	M. p. (°C)	B. p. (°C/mm)	Sp. gr. $^{25}/_{4}$	n_D^{25}	Solv in H_2O g/100g soln
α-Methyl		136/40 220/760	1.111	1.442	∞
β-Methyl		148/40 232/760	1.124	1.446	∞
α,β-Dimethyl		100/40 180/760	1.016	1.421	∞
α,γ-Dimethyl		88/40 169/760	1.004	1.417	∞
α,β,γ-Trimethyl		148/760	0.937	1.401	∞
α-Ethyl		112–3/10 220/760	1.063	1.441_D^{20}	∞
α,γ-Diethyl		108–111/60	0.953	1.420	∞
α,β,γ-Triethyl		103–5/60 181/760	0.886	1.407	10
α-,n-Propyl		118–122/15	1.074_4^{18}	1.440_D^{18}	
α,γ-Di-n-propyl		135–7/60 218/760	0.927	1.424	8
α,γ-Di-isopropyl		123–4/60 199/760	0.914	1.418	20
α-n-Butyl		133–7/18	0.945_{25}^{25}	1.446_D^{18}	
α-Isobutyl		110–2/4	0.991	1.437	
α-Isoamyl		136–8/10 254/760	0.976		1
α,γ-Di-isoamyl		120–1/4 265/760	0.901	1.431	1
α-Phenyl	54, 68	150–5/4			
β-Phenyl	68				
α,γ-Diphenyl	80–1	287–8/760			
α-Benzyl		164–6/2	1.130	1.530	1
α,γ-Dibenzyl		198–204/2–3	1.100	1.547	insol.
α-(o-Tolyl)	69–70				
α,γ-(Di-o-tolyl)		195–7/2	1.111	1.556	insol.
α-(m-Tolyl)	65				
α,γ-(Di-m-tolyl)		205–7/2	1.105	1.558	insol.
α-(p-Tolyl)	73–4				
α,γ-(Di-p-tolyl)	88				insol.
α-(α-Naphthyl)	91–2				slight
α-(β-Naphthyl)	109–10				slight
α-Trityl	93–4 108–10				
α,β-Dityrityl	170–1				
α,β,γ-Tritrityl	196–7				
α-Oleyl (Selachyl alc.)	17.6–19		$0.923_4^{22.5}$	1.471_D^{22}	



When dichlorohydrin is used, two epoxy rings are successively formed and opened and a diether is produced[92].

An alternate method of producing glycerol ethers is the reaction of sodium glyceroxide with an alkyl or aryl bromide or alkyl sulfate.[93] Glycerol ethers may be prepared from glycidol, epichlorohydrin or a glycidol ether by treatment with an alcohol or a phenol. The reaction is catalyzed by either acid or alkali[94].

The glycerine molecule can react with other alcohols to form aliphatic or aromatic ethers, or as pointed out before with itself to form polyglycerols as:



These aliphatic and aromatic ethers cover a wide range of physical properties and are useful as solvents and chemical intermediates.

SULFUR COMPOUNDS

Sulfur can replace one or more of the oxygen atoms of glycerol to form a series of sulfur analogues, the thioglycerols. The sulfhydryl groups in these compounds are much more reactive than the corresponding hydroxyl groups. They are easily oxidized and are subject to condensation reactions, which form glycerol sulfides or thioethers, analogous to the polyglycerols. They also form sulfides by reaction with glycidol or epichlorohydrin.

Alpha - thioglycerol $HS-CH_2-CHOH-CH_2OH$ is a

colorless, viscous liquid with only a slight odor when pure. It is soluble in water in all proportions, easily soluble in alcohol and acetone, and slightly soluble in ether and benzene. It may be prepared from glycerol monochlorohydrin and a 10% excess of potassium hydrosulfide, or a 25% excess of sodium hydrosulfide in alcohol[95]. A third method of preparation is by the reaction of glycidol and hydrogen sulfide in the presence of barium hydroxide. Dithioglycerol and trithioglycerol may be prepared from sodium hydrosulfide and glycerol di-, or trichlorohydrin respectively[96].

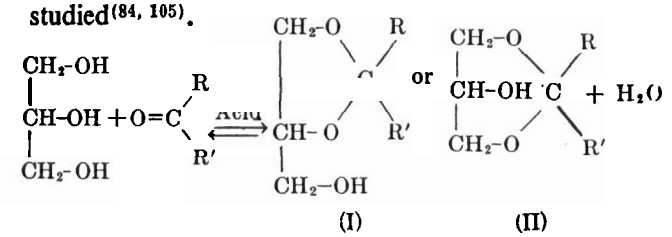
GLYCEROL AMINES

Glycerol amines are formed by the replacement of one or more of the hydroxyls by amine groups. They are basic compounds, generally water soluble and hygroscopic. With fatty acids they form soaps that are soluble in organic solvents[97]. The glycerol mono-, and diamines are readily made from the corresponding chlorohydrins or bromohydrins, while the triamine is usually prepared from non glycerol origins.

When a glycerol halohydrin and ammonia react, it is possible for a number of products to be formed. Each of the ammonia hydrogens can react, so mono-, di-, and triglycerol amines can be formed. If a dihalohydrin is used, the number of possible products is increased by the opportunity for the formation of long-chain molecules and cross-linkages. Insufficient ammonia favors the formation of such complex products. They are nonvolatile and vary from viscous liquids to more or less solid materials[98]. The preparation of simple glycerol amines, the diamines and the triamines is described in several sources[99, 100, 101, 102, 103, 104].

GLYCEROL ACETALS

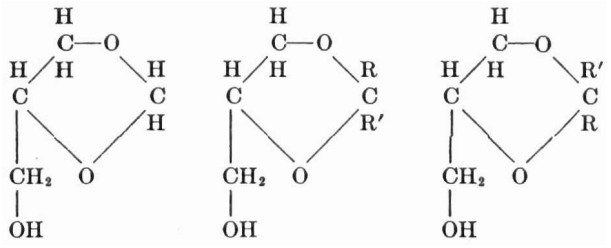
The acetals of glycerol, formed by the condensation of glycerol with aldehydes and ketones are heterocyclic compounds that show structural, geometric and optical isomerism. They are formed by the condensation of two hydroxyls of a glycerol molecule with the carbonyl of an aldehyde or a ketone. The reaction is catalyzed by acid and is an equilibrium reaction, sensitive to the presence of water. These isomers have been very thoroughly studied[84, 105].



(I) (II)

Temperature plays an important role in determining the ratio of isomeric acetals formed. It is believed the ring fission occurs under the influence of the acid catalyst and that the reaction then goes to equilibrium, which is dependent on the temperature. Higher temperatures favor formation of the 5 membered ring and lower temperatures favor formation of the 6 membered ring[106].

Geometric isomerism occurs in the acetals, except in certain ones, such as methylidene glycerol, which lack the necessary asymmetry. This is shown in the following structural formulas of compounds having 5 membered rings. Compounds with six membered rings are analogous.



α,β-Methylidene glycerol *Geometric isomers*

The two geometric isomers of each of the structural isomers of para-nitro benzylidene glycerol were isolated by Hibbert and Sturrock[107] but their configuration was not established. The geometric isomers of alpha, gammabenzylidene glycerol were separated by Verkade and van Roon[108].

The principal method of preparing glycerol acetals is by the condensation of glycerol with an aldehyde or ketone in the presence of an acid or an acid salt. If the carbonyl compound is comparatively cheap as compared with glycerol, or may be easily removed, it is ordinarily used in large excess, as much as 4 or 5 moles to 1 mole of glycerol. Various acids and acid salts have been tried as catalysts. Hydrochloric acid or sulfuric is frequently used, the amount being in the order of one percent or less based on the glycerol.

Glycerol and other alcohols can be converted into acetals by combination with vinyl ethers, preferably in the presence of an acid catalyst and in a solvent such as ether or chloroform[109].

The ease with which acetals are formed is influenced by the polar character of the carbonyl group. As it becomes more negative, the ease of formation and the stability of the intermediate product (a hemiacetal) increases but the completion of the reaction with closure of the ring becomes more difficult[110, 106].

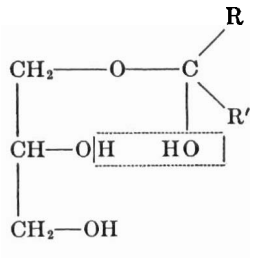
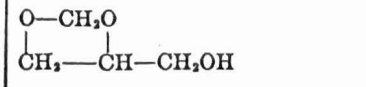
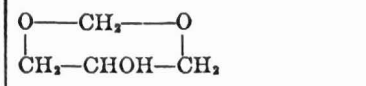
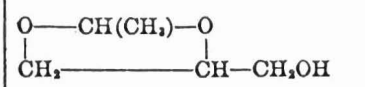
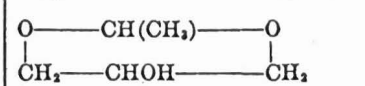
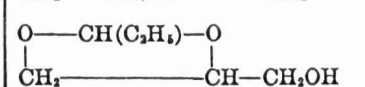
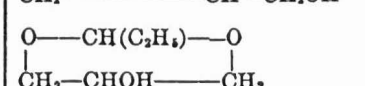
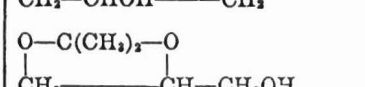
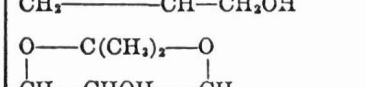
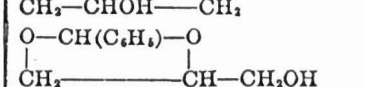
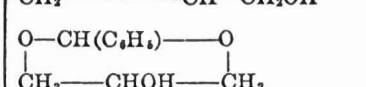
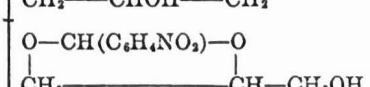
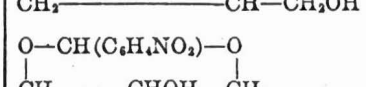


TABLE 4. PHYSICAL PROPERTIES OF SOME GLYCEROL ACETALS

Name	Formula	B.P. °C/mm	d (°C)	n_D (°C)
α,β-Methylidene glycerol		84–5/11	1.2113 (20)	1.4477 (20)
α,γ-Methylidene glycerol		82/11	1.2256 (20)	1.4533 (20)
α,β-Ethylidene glycerol		68–70/1	1.1243 (17)	1.4413 (17)
α,γ-Ethylidene glycerol		52/1	1.1477 (17)	1.4532 (17)
α,β-Propylidene glycerol		70–2/3	1.0767 (25)	1.4424 (25)
α,γ-Propylidene glycerol		50–1/2	1.0889 (25)	1.4448 (25)
α,β-Isopropylidene glycerol		82.5–83/13	—	—
α,γ-Isopropylidene glycerol		90–1/13	1.0911 (20)	1.4427 (20)
α,β-Benzylidene glycerol		143–4/2	1.1916 (17)	1.5389 (17)
α,γ-Benzylidene glycerol		83.5*	—	—
α,β-p-Nitrobenzylidene glycerol		177–9/0.3	—	—
α,γ-p-Nitrobenzylidene glycerol		88 or 95–8*	—	—

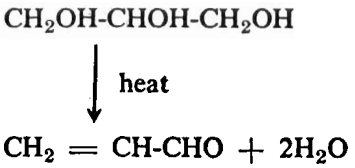
* Melting point.

The physical properties of some of the acetals of glycerol are given in table 4. Only structural isomerism is considered here.

Acetals and ketals of glycerine have applications as solvents and plasticizers and since they are easily hydrolyzed are a potential source of reactive groups.

DEHYDRATION AND PYROLYSIS

Dehydration of glycerol may form a number of products, but the principal is acrolein —



The reaction is the basis of several quantitative tests for glycerol. Acrolein and aldehyde condensation products are formed when glycerol vapors are passed over alumina at 360° C. Finely divided copper at 330° C. causes glycerol to decompose to acrolein, allyl alcohol, ethyl alcohol, hydrogen and small amounts of carbon monoxide. Other catalysts will cause breakdowns of glycerol to the above products in different proportions.

Glycerol is also fermented to acrolein by B. amaracrylis, the organism which produces bitterness in wine.[111]

COMPOUNDS WITH BASES AND SALTS

Glycerol reacts readily with alkalies, alkaline earths and some metallic oxides to form glyceroxides which are analogous to the alcoholates, and are generally stable only in the presence of an alkali. Lead glyceroxide, formed from litharge and glycerol, is relatively insoluble and stable.

$$C_3H_5(OH)_3 + PbO \rightarrow C_3H_5(OH)O_2Pb + H_2O$$

The reaction is exothermic. Although amorphous at first, the compound soon changes to minute fibrous crystals which radiate from the particles or unreacted litharge and bind the whole into a very hard mass[112, 113]. The percentage of water, pH, and freshness of the litharge all affect the rate of hardening of the cement.[90, 114, 115].

When glycerol reacts with bases and salts either an alpha or beta hydroxyl group may react, but the former reacts more readily[116].

Sodium glyceroxide is easily prepared by heating and stirring together equimolar quantities of powdered sodium hydroxide and glycerol. The reaction is exothermic and becomes very rapid at temperatures above about 140° C.

$$CH_2OH - CHOH - CH_2OH + NaOH \rightarrow$$

$$NaOCH_2 - CHOH - CH_2OH + H_2O$$

External heat is required to remove the last of the water formed and force the reaction to completion. Sodium glyceroxide does not melt but decomposes at 235° C. It can also be prepared from glycerol and an excess of metallic sodium in absolute alcohol[117, 118] and from the same two chemicals in liquid ammonia[119]. Potassium glyceroxide is prepared like sodium glyceroxide and has similar properties[120].

Disodium glyceroxide may be prepared from monosodium glyceroxide and one equivalent of sodium ethylate – at high temperatures[121].

Glycerol in aqueous solution is decomposed by alkali at high temperatures and pressure. At 550° F. (288° C.) there is about 4% destruction of glycerol in a 7 minute period for each percent of sodium hydroxide in the solution. Loss of glycerol in the presence of sodium carbonate is only about one tenth as great as with sodium hydroxide. Decomposition is proportional to time and double for each 25° F. increase in temperature. Substitution of nitrogen for air in the system reduces the loss of glycerol[122].

Glycerol forms molecular addition compounds with alkaline earth hydroxides and many of their salts[123, 124]. Many metals, in addition to those of the alkaline earths group, form compounds with glycerine. Most of these are soluble in water or alkaline solution and this provides a means of making alkaline solutions of the metals. The amount of cupric hydroxide which will dissolve in alkaline glycerol increases with the concentration of alkali[125].

$$C_3H_5(OH)_3 + NaOH \rightleftarrows C_3H_5(OH)_2ONa + H_2O$$

This in turn reacts with cupric hydroxide.

$$2C_3H_5(OH)_2ONa + Cu(OH)_2 \rightleftarrows [C_3H_5(OH)_2O]_2Cu + 2NaOH$$

Thus glycerol can be substituted for sodium-potassium tartrate in Fehling's solution[126]. Complex compounds containing two metals such as barium, strontium, calcium, iron, aluminum, chromium, antimony or bismuth may be prepared from glycerol, alkali and the appropriate metal salt,[127, 128, 129].

When a solution of a copper salt, except cupric chloride, in glycerol is heated to 150-200° C., a vigorous reaction occurs and finely divided metallic copper is produced. The copper is suitable for use as a catalyst. With cupric chloride, crystalline cuprous chloride is produced[130].

Reaction with Diisocyanates

Propylene oxide alone, or with some ethylene oxide, added to glycerine produces tri-functional polymers of 1000 to 4000 molecular weight. The tri-functionality of these polyethers, provides the ability to produce cross-linked flexible urethane foams, on reaction with diisocyanates. The reaction can be in the form of a one-shot process, where approximate chemical equivalents of the polyether and diisocyanate are reacted, or by the preparation of a prepolymer by partial reaction of a polyether with an excess of diisocyanate. In the latter case, the foam is produced by the addition of water, catalysts, and modifiers.

Also, by reaction with diisocyanates such as tolylene diisocyanate, pre-polymers can be prepared and blocked with phenol for baking enamels; or the pre-polymers can be cured with other polyols, amines, or air/moisture to give urethane coatings.

MISCELLANEOUS

Pyrene and glycerol condense easily in the presence of sulfuric acid to give $C_{19}H_{10}O$. The glycerol is first dehydrated to acrolein and this in turn reacts with the pyrene[132].

Similar condensations have been accomplished with other aromatic compounds.

When 1- or 2-aminoanthraquinone reacts with glycerol and sulfuric acid, 2, 3-pyridinoanthraquinone is formed; yellow needles from aniline, m.p. 322° C.

Anthrol, glycerol and sulfuric acid at 120° C., or anthraquinone, glycerol and aniline sulfate at 100° C., give benzanthrone[133].

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