[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XXIII. SYNTHESIS AND PROPERTIES OF HYDROXY ALKYLIDENE GLYCOLS AND GLYCEROLS

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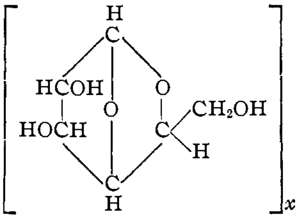
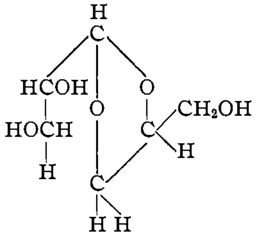
Investigations dealing with a study of cyclic acetal formation during recent years have dealt almost exclusively with cyclic acetals prepared from saturated derivatives. The tendency of unsaturated aldehydes toward cyclic acetal formation has been but little investigated. The study of this type of cyclic acetal apparently has been rendered difficult by the fact that unsaturated aldehydes, in general, condense only with difficulty with polyhydric alcohols under the experimental conditions usually employed. The use of acid catalysts is disadvantageous, due in many cases to polymerization of the aldehyde. The difficulty appears to lie in the securing of the optimum hydrogen-ion concentration, and failure to undergo condensation may be due to this, coupled with low reaction velocity between the aldehyde and polyhydroxy derivative.

The possibility that the lignin complex, as it occurs in wood, may contain an unsaturated aldehyde grouping,[2] which may be combined with a carbohydrate complex in the form of a cyclic acetal or half acetal, pointed to the necessity for obtaining further information regarding the interaction of unsaturated aldehydes with polyhydric compounds.

Also of added interest is the close connection, as indicated in a previous communication,[3] between cellulose considered as an anhydroglucose (A) and 1,2-dihydroxypropylidene-glycerol-1,2 (2-dihydroxy-ethyl-1,3-dioxolane-4-carbinol) (B), *e. g.*



(A)



(B)

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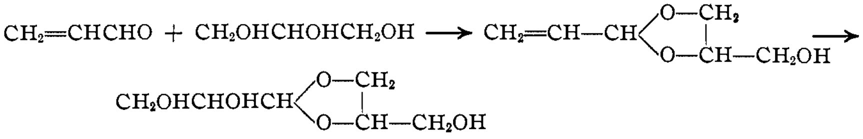
[1] Holder of studentship, Canadian National Research Council. The authors wish to express their thanks to the Canadian National Research Council and the Canadian Pulp and Paper Association for the generous support accorded to them.

[2] Fuchs, "Die Chemie des Lignins," J. Springer, Berlin, **1926**, pp. 277–285.

[3] Hibbert and Whelen, THIS JOURNAL, **51**, 620 (1929).

For these reasons it seemed of interest to prepare the cyclic acetals involving condensation of acrolein with glycol and glycerol, namely, acrylidene glycol and glycerol, and to use these as initial materials from which, by oxidation, the corresponding dihydroxy derivatives could be obtained

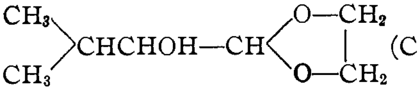
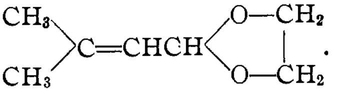


$$CH_2{=}CHCHO + CH_2OHCHOHCH_2OH \longrightarrow CH_2{=}CH{-}CH\left\langle\begin{matrix}O{-}CH_2\\ \;|\\ O{-}CH{-}CH_2OH\end{matrix}\right. \longrightarrow$$

$$CH_2OHCHOHCH\left\langle\begin{matrix}O{-}CH_2\\ \;|\\ O{-}CH{-}CH_2OH\end{matrix}\right.$$

(B)

in order to ascertain how far such structures exhibit a tendency toward polymerization or association.

Investigations on unsaturated cyclic acetal formation have been very limited. Lochert,[4] in an attempt to prepare α-hydroxy-*iso*-amylidene glycol,  $\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>\!CHCHOH{-}CH\left\langle\begin{matrix}O{-}CH_2\\ |\\ O{-}CH_2\end{matrix}\right.$ (C), by the saponification of α-bromo-*iso*-amylidene glycol, secured a very small amount of what he believed to be the desired compound, (C), but as was to be expected the bulk of the reaction product was the unsaturated cyclic acetal, β-methylcrotonylidene glycol, [2 - (β - methylpropene - 2) - 1,3 - dioxolane],  $\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>\!C{=}CHCH\left\langle\begin{matrix}O{-}CH_2\\ |\\ O{-}CH_2\end{matrix}\right.$. No investigation of the chemical properties of the unsaturated acetal was made and the presence of α-hydroxy-*iso*-amylidene glycol was not definitely established.

Peacock[5] was the first to prepare cinnamylidene glycerol, and its preparation, properties, etc., have been studied more fully by the present authors.[3]

More recently several unsaturated aldehydes have been condensed with glycol by Hibbert and co-workers[6] to give unsaturated cyclic acetals.

As far as can be ascertained the literature contains no reference to the condensation of acrolein with glycol, and the authors' experiments to bring about such a condensation were unsuccessful. It was, however, possible to prepare the desired acrylidene glycol by indirect synthesis.

The condensation of acrolein and glycerol was first carried out by Nef,[7] who in a study of the dehydration of glycerol isolated a material which he considered to be acrylidene glycerol, though he did not make a detailed investigation of it nor did he establish its identity.

In the present investigation it is shown that the product obtained on heating acrolein with glycerol, without a catalyst, under low pressure, is

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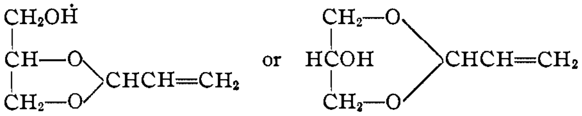
[4] Lochert, *Ann. chim. phys.*, [6] **16**, 26 (1889).

[5] Peacock, *J. Chem. Soc.*, **107**, 816 (1915).

[6] Hibbert, Houghton and Taylor, THIS JOURNAL, **51**, 611 (1929).

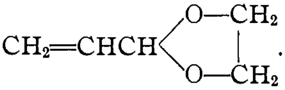
[7] Nef, *Ann.*, **335**, 224 (1904).

an acrylidene glycerol which is identical with the material isolated by Nef. This author pointed out that his material could be either of two products (D or E)



(D) (E)

The present investigation shows that the condensation apparently gives rise to only the five-membered acetal (D). From the point of view of Michael's partition principle the second isomer is probably formed but either in quantity too small to be isolated, or, if in larger amount, it possibly undergoes spontaneous polymerization and remains in the thick, viscous, undistillable residue which is always left in large quantity.

It will be readily observed that with acrylidene glycol only one ring system is possible, namely,  $CH_2{=}CHCH\langle(O{-}CH_2)(O{-}CH_2)$. This product was obtained by indirect synthesis as shown in the experimental part.

These .products, acrylidene glycol and glycerol (after determination of the structure of the latter), were then used as convenient starting materials for the preparation of the corresponding dihydroxy derivatives, this being accomplished by oxidation with potassium permanganate at a low temperature.

Of the two dihydroxy acetals thus obtained, the former represents the first cyclic acetal of glycerol to be synthesized containing hydroxyl groups in the alkylidene side chain. It will be observed that they represent the condensation of a simple sugar with a polyhydric alcohol.[8]

The direct condensation of acrolein and ethylene glycol to form acrylidene glycol (2-allyl-1,3-dioxolane) does not take place readily enough to form the basis of a practical method of preparation. The use of catalysts such as anhydrous copper or sodium sulfate, and variation of the experimental conditions, did not appreciably aid the reaction. Catalysts with an acid reaction were precluded due to their action in bringing about a polymerization of the acrolein. Accordingly, the method used was one of indirect synthesis and was an application of that used by Wohl,[9] as modified by Witzemann,[10] for the preparation of open-chain acetals. This slightly modified procedure consisted in dropping acrolein into a solution of hydrogen chloride in ethylene glycol at a temperature of 0 to +5°, the following change taking place.

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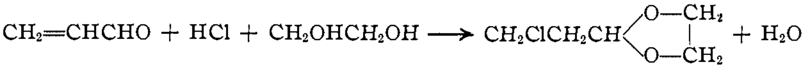
[8] Hydrolysis of this compound should readily yield glyceric aldehyde as one product, although this phase of the subject was not investigated.

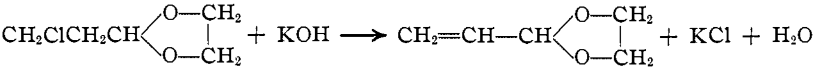
[9] Wohl, *Ber.*, **31**, 1797, 2394 (1898); **33**, 3095 (1900).

[10] Witzemann, THIS JOURNAL, **36**, 1766, 1908 (1914).



$$CH_2{=}CHCHO + HCl + CH_2OHCH_2OH \longrightarrow CH_2ClCH_2CH\left\langle\begin{array}{l}O-CH_2\\ \quad\ |\\ O-CH_2\end{array}\right. + H_2O$$

The reaction mixture was poured into water, the oily layer separated, taken up in ether, dried and fractionated under reduced pressure. The β-chloropropylidene glycol (2-β-chloro-ethyl-1,3-dioxolane) so obtained was heated with dry, powdered potassium hydroxide in order to convert it into acrylidene glycol



$$CH_2ClCH_2CH\left\langle\begin{array}{l}O-CH_2\\ \quad\ |\\ O-CH_2\end{array}\right. + KOH \longrightarrow CH_2{=}CH-CH\left\langle\begin{array}{l}O-CH_2\\ \quad\ |\\ O-CH_2\end{array}\right. + KCl + H_2O$$

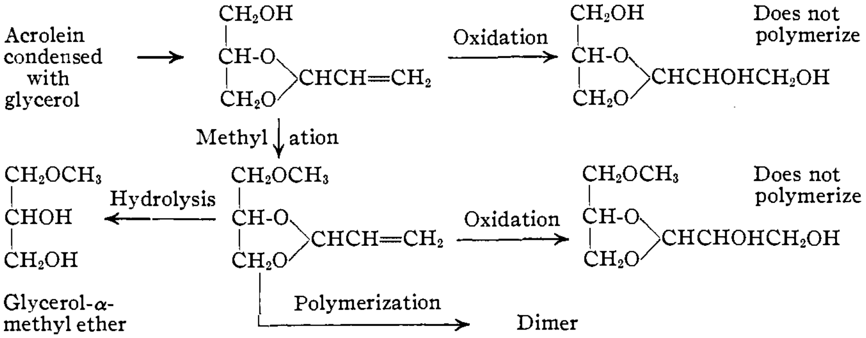
The conversion of acrylidene glycol to 1,2-dihydroxypropylidene glycol (2-dihydroxy-ethyl-1,3-dioxolane) was accomplished by oxidizing with potassium permanganate at a low temperature, removal of the precipitated manganese dioxide, concentration of the slightly alkaline aqueous solution and distillation under low pressure.

Dihydroxypropylidene glycol, as isolated, is a clear liquid with a viscosity approximating to that of ethylene glycol. It burns vigorously when ignited, giving a non-luminous flame. It is quite stable on distillation under reduced pressure and shows no tendency to polymerize under prolonged heating with, or without, non-acid catalysts.

Acrylidene glycerol was prepared by the direct condensation of acrolein and glycerol without a catalyst. The only product isolated from the reaction mixture was shown to possess the five-membered cyclic structure (D) by the usual methylation and hydrolysis technique. No product indicating the presence of the isomeric six-membered acetal could be found. There was always, however, a very large quantity of a thick, viscous, dark brown oil left in the reaction flask, which probably consisted of unchanged glycerol, polyglycerols, polymerized acrolein and possibly a polymerized six-membered cyclic acetal of acrolein and glycerol. No method could be found permitting of the isolation of the individual components.

1,2-Acrylidene-glycerol (2-allyl-1,3-dioxolane-4-carbinol), prepared as above, is a clear liquid of relatively low viscosity, possessing a distinct and somewhat strong odor. It has a marked tendency to hydrolyze, with evolution of acrolein, in dilute aqueous acid solution, especially when warmed. It is monomolecular and shows no tendency toward polymerization. On the other hand, its methyl ether (1,2-acrylidene-glycerol-1′-methyl ether) was found to be a mobile liquid of somewhat pleasant odor, monomolecular when first prepared, but changing after standing for several months into a very viscous product, the composition of which corresponded approximately to that of a dimer. It is possible that this change is due to association, or it may be the result of aggregation involving the migration of a hydrogen atom from one part of the molecule to the double linkage, with subsequent ring closure and polymerization. An interesting comparison is to be found in the fact that acrylic acid ($CH_2=CHCOOH$) shows little or no tendency to polymerize, while with ethyl acrylate ($CH_2=CH-COOC_2H_5$) this tendency is very pronounced.

Both 1,2-acrylidene-glycerol-α-methyl ether and 1,2-acrylidene-glycerol were subjected to oxidation by aqueous permanganate to convert them into the corresponding dihydroxy compounds; thus prepared these were very viscous, high-boiling liquids. They were monomolecular and showed no tendency toward polymerization either under the influence of heat or non-acid catalysts. Distillation of the 1,2-acrylidene-glycerol, however, always left a considerable quantity of a caramel-like, dark brown residue, the nature of which could not be determined. The course of these reactions may be shown as follows



Experimental

Preparation of β-Chloropropylidene Glycol (2-(β-Chloro-ethyl)-1,3-dioxolane).—Eighty grams of acrolein was allowed to drop slowly, with vigorous stirring, into a solution of 40 g. of hydrogen chloride dissolved in 120 g. of ethylene glycol. The temperature was carefully maintained by means of a freezing mixture at 0 to +4°. If this precaution was not taken the heat of reaction was such that much of the acrolein was polymerized. The reaction mixture was allowed to stand for two hours at room temperature and then poured into a liter of cold water. The β-chloropropylidene glycol separated as an oily layer. It was removed in a separatory funnel, taken up in ether, dried over anhydrous sodium sulfate and fractionated under reduced pressure, yielding 70 g. of a clear, colorless liquid, b. p. 70–72° (18 mm.). A small residue (which was probably polymerized acrolein or β-chloropropionaldehyde) remained in the distillation flask.

β-chloropropylidene glycol on standing gradually turns dark brown in color. When warmed with dilute aqueous acid, a very obnoxious odor, even more offensive than that of acrolein, is evolved, which in all probability is β-chloropropionaldehyde produced by the hydrolysis of the acetal.

Preparation of Acrylidene Glycol (2-Allyl-1,3-dioxolane).—The preparation of acrylidene glycol involved the removal of hydrogen chloride from β-chloropropylidene glycol. Dry powdered potassium hydroxide was used for this purpose.

To six times the theoretical quantity of very finely-powdered potassium hydroxide (124 g.), placed in a round-bottomed copper flask fitted with a short distilling column and condenser, was added 50 g. of β-chloropropylidene glycol. A marked rise in temperature occurred and the mixture was then slowly heated over a free flame until distillation took place. A clear liquid, b. p. 115–119°, was obtained, which on redistillation yielded usually about 20 g. of acrylidene glycol, b. p. 115–116°. Yields from various 50-g. lots averaged approximately 50%.

Excess potassium hydroxide was used in these preparations to absorb the water formed in the reaction. If the latter is allowed to remain uncombined, some of the β-chloropropylidene-glycol undergoes hydrolysis to β-chloropropionaldehyde. A small amount of this compound escapes polymerization by the hot alkali (probably being formed in the vapors above the alkali) and passes over with the distillate giving it an extremely lachrymatory odor, even more pronounced than that of acrolein. Whenever this was formed the yield of acrylidene glycol was always somewhat lower. Acrolein odors were also sometimes present.

If the reaction is carried out in glass flasks great care must be taken to avoid accidents liable to result from the leaking of hot alkali from a cracked flask. For this reason it was found more satisfactory to use a copper vessel.

Acrylidene glycol is a clear, colorless, very mobile and volatile liquid possessing a somewhat strong, sweetish, slightly unpleasant odor. When hydrolyzed by warming with dilute acid, acrolein is readily evolved.

Anal. Calcd. for $C_5H_8O_2$: C, 60.00; H, 8.00. Found: C, 59.28; H, 7.84.

Preparation of 1,2-Dihydroxypropylidene-glycol (2-Dihydroxyethyl-1,3-dioxolane).—The oxidation of acrylidene glycol to 1,2-dihydroxypropylidene glycol was accomplished by allowing a nearly saturated solution of potassium permanganate to drop into a suspension of acrylidene glycol in water.

Eight hundred and twenty cc. of an aqueous solution containing 42.1 g. of potassium permanganate was added to 40 g. of acrylidene glycol suspended in 400 cc. of water and contained in a three-necked liter flask, the addition being made at the rate of approximately 20 cc. per minute, the mixture being cooled by an ice-bath and vigorously agitated by a mechanical stirrer. The initial temperature was about 9°. After commencement of the reaction the temperature was allowed to fall and then maintained below 5° throughout the addition. The reaction mixture was kept in an ice-bath for two hours, then heated to 90° in a water-bath, the manganese dioxide separated by filtration and the water removed from the aqueous, slightly alkaline filtrate by distillation under reduced pressure at 28° until the volume was approximately 50 cc. The residual liquid was filtered and fractionated; yield, 22 g. (41%) of a viscous, clear, colorless liquid; b. p. 136–138 (5 mm.); n_D^{17} 1.4695.

Anal. Calcd. for $C_5H_{10}O_4$: C, 44.77; H, 7.46. Found: C, 44.38; H, 7.17. Mol. wt. (ethylene bromide). Calcd.: 134. Found: 140.

It is to be noted that the above distillation was carried out using the alkaline solution formed in the oxidation in order to avoid hydrolysis of the acetal.

Preparation of 1,2-Acrylidene-glycerol (2-Allyl-1,3-dioxolane-4-carbinol).—One hundred and twelve grams (2 moles) of acrolein and 184 g. (2 moles) of glycerol were placed in a pressure bottle and heated for several weeks under pressure at a temperature of 50–60°. Placing the bottle on a warm radiator was found to be satisfactory. On first mixing, the two substances were immiscible, but after heating for several days a homogeneous solution resulted. Various experiments were carried out and it was found that the longer the heating was continued, the better was the yield. The reaction mixture was then distilled under reduced pressure. Usually very little unchanged acrolein remained and the distillate boiling under 165° (10 mm.) was collected separately. A very large quantity of a thick, viscous, undistillable liquid remained which probably contained unchanged glycerol, polyglycerols and various polymerized products. The distillate on fractionation gave a clear oil, b. p. 204–215°; (98–105°, 10 mm.); n_D^{17} 1.4638. It was further refractionated into two fractions, (1) b. p. 204–208°, and (2) b. p. 208–

215°. Both of these reacted as strongly unsaturated substances toward bromine and potassium permanganate, and on warming with dilute acid evolved acrolein very readily. The odor of the fractions when first prepared was marked but not unpleasant; on standing, the odor of acrolein was noticeable due to slight hydrolysis. Yields from a number of experiments averaged between 10 and 15%.

Anal. (Fraction b. p. 98–105°, 10 mm.). Calcd. for $C_6H_{10}O_3$: C, 55.44; H, 7.67. Found: C, 55.40; H, 7.87. Mol. wt. (ethylene bromide). Calcd.: 130. Found: 132.

Determination of Structure.—Both of the above fractions (1) and (2) yielded the same acrylidene-gylcerol-α-methyl ether, the wide range in boiling point possibly being due to the presence of *cis* and *trans* isomers.

The usual methylation–hydrolysis method was employed and it was found that the acrylidene glycerol as isolated above consisted only of the five-membered acetal. The six-membered acetal either was not formed in sufficient quantity for isolation or it was polymerized and remained in the residue from the reaction.

Methylation of 1,2-Acrylidene-glycerol.—Fifty grams of acrylidene glycerol, b. p. 98–102° (10 mm.), was methylated in the usual manner, using 200 g. of methyl iodide and 120 g. of silver oxide. The reaction mixture was extracted with ether, dried with anhydrous sodium sulfate, and fractionated under reduced pressure; 38 g. of acrylidene-glycerol-α-methyl ether, b. p. 70° (13 mm.), (174–178°, 760 mm.), n_D^{17} 1.4408, was obtained. Nine and six-tenths grams of 1,2-acrylidene glycerol, b. p. 204–207°, was also recovered.

Acrylidene-glycerol-α-methyl ether is a mobile liquid, monomolecular when first isolated, and possessing a somewhat pleasant, ethereal odor. However, after standing for several months it became very viscous in character and a molecular weight determination showed it had been almost completely converted into a dimer. No hydrolysis had taken place during this period.

Methylation of the other fraction of acrylidene-glycerol, b. p. 208–215°, gave only acrylidene-glycerol-α-methyl ether, b. p. 174–178°.

The identity of the material in question was proved by (a) the formation of glycerol-α-methyl ether on hydrolysis, and (b) its conversion into 1,2-dihydroxypropylidene-glycerol-1′-methyl ether on oxidation.

Mol. wt. of freshly prepared acrylidene-glycerol-α-methyl ether in ethylene bromide, calcd.: 144. Found: 145. *Mol. wt.* of above compound after standing (ethylene bromide). Found: 273.

Hydrolysis of Acrylidene-glycerol-α-methyl Ether.—Seven grams of acrylidene-glycerol-α-methyl ether (b. p. 174–178°) was hydrolyzed by boiling under a reflux condenser for seventy minutes with 25 cc. of 75% aqueous ethyl alcohol containing 0.5% hydrochloric acid. Acrolein was evolved vigorously and was removed by applying gentle suction to the top of the condenser. The reaction mixture was neutralized with lead carbonate, filtered, concentrated and the residue distilled under reduced pressure, yielding only glycerol-α-methyl ether, b. p. 110–112° (13 mm.), n_D^{17} 1.4465, and thus serving to identify the structure of the original product as the five-membered acrylidene glycerol, (D).

Preparation of 1,2-Dihydroxypropylidene-glycerol-1′-methyl Ether.—The simplest and most dependable mode of synthesis appeared to lie in the oxidation of acrylidene-glycerol-α-methyl ether to the corresponding dihydroxy compound. By protecting the α-hydroxyl group by a prior methylation, it was thought that any secondary oxidation might be avoided. Moreover, this would yield a new type of cyclic acetal ether.

Thirty grams of acrylidene-glycerol-α-methyl ether was suspended in 300 cc. of water and oxidized in the usual manner with 560 cc. of an aqueous solution containing 29.5 g. of potassium permanganate. The water was removed from the filtered, slightly alkaline solution by distillation under reduced pressure. The residual oil on fractionation and refractionation yielded 9.4 g. of a heavy, slightly yellowish liquid, b. p. 146° (1–2 mm.), $n_{\rm D}^{17}$ 1.4680. Analysis showed it to be 1,2-dihydroxypropylidene-glycerol-1′-methyl ether.

Anal. Calcd. for $C_7H_{14}O_5$: C, 46.54; H, 7.92. Found: C, 46.56; H, 7.98. Mol. wt. (ethylene bromide). Calcd.: 178. Found: 197.

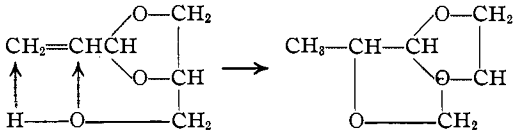
The product shows no tendency to polymerize either on heating or under the influence of non-acid catalysts such as alkalies, aluminum alkylates, etc.

Synthesis of 1,2-Dihydroxypropylidene-glycerol (1,2) (1,2-Dihydroxy-ethyl-1,3-dioxolane-4-carbinol).—Twenty-five and five-tenths grams of 1,2-acrylidene-glycerol (b. p. 204–207°) was dissolved in 250 cc. of water and oxidized with a solution containing 20.7 g. of potassium permanganate in 365 cc. of water under the same conditions that were employed in the preceding experiment. The reaction product after filtration, but without neutralizing, was concentrated under reduced pressure. The residual oil on fractionation yielded 3 fractions—(1) 8 g. of a clear oil, b. p. 54° (2 mm.); (2) a small quantity of unchanged acrylidene-glycerol, b. p. 70° (2 mm.); and (3) 2.8 cc. of a very viscous, slightly yellow-colored liquid, b. p. 200–204° (5 mm.), $n_{\rm D}^{17}$ 1.4888, proved by analysis to be 1,2-dihydroxypropylidene-glycerol (1,2-) and which could be redistilled unchanged. A large, undistillable, tarry, caramel-like residue remained.

The identity of Fraction I, b. p. 54° (2 mm.), was not determined. It behaved as a saturated substance toward potassium permanganate and bromine and also reacted with metallic sodium. On warming with dilute acid an aldehyde was evolved, the identity of which was not determined.

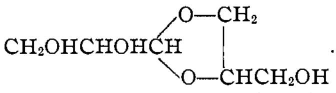
Anal. of Fraction (*3*). Calcd. for $C_6H_{10}O_3$: C, 55.44; H, 7.67. Mol. wt., 130. Found: C, 55.40; H, 8.00. Mol. wt. (ethylene bromide), 124.

It is possible that the product represents a bicyclic acetal formed by the wandering of a hydrogen atom, as indicated



The product is at present under investigation. If this mechanism should prove correct, the reaction would form an interesting example of the wandering of a hydrogen atom to a vinyl radical in an *alkaline* medium.

1,2-Dihydroxypropylidene-glycerol (1,2),



$$CH_2OHCHOHCH\begin{matrix} O—CH_2 \\ | \\ O—CHCH_2OH \end{matrix}$$

.—1,2-Dihydroxypropylidene-glycerol-1,2 is monomolecular, and as far as could be determined, shows no tendency to polymerize on heating with, or without, non-acid catalysts. During its preparation a large quantity of residue remained and it was thought that a better yield could be obtained by carrying out the distillation at a very low pressure. However, distillation at 0.15 mm. (using a Hyvac and mercury vapor pump) gave no better results, the reaction product yielding only 2 g. of dihydroxypropylidene-glycerol (1,2), b. p. 146° (0.15 mm.). A considerable amount of a caramel-like substance again remained but it was impossible to determine whether this represented a polymerization or a decomposition product.

Anal. of 1,2-Dihydroxypropylidene-glycerol (1,2). Calcd. for $C_6H_{12}O_5$: C, 44.77; H, 7.46; mol. wt. 163. Found: C, 44.38; H, 7.17; mol. wt. (acetone), 156.

Attempts to Bring about Polymerization.—1,2-Dihydroxypropylidene-glycerol

(1,2) was heated for several weeks at 110° with non-acid catalysts such as potassium hydroxide, and sodium and aluminum ethylates, but no tendency to polymerize was observed. Likewise, heating for long periods at 110° without a catalyst, or exposure to sunlight in a quartz glass tube, had no effect.

The close relationship of 1,2-dihydroxypropylidene-glycerol (1,2) to the cellulose nucleus was previously pointed out,[3] and it would seem that polymerization does not take place unless ring closure has been previously effected.

Summary

1. Two new unsaturated cyclic acetals, namely, acrylidene-glycol and acrylidene-glycerol have been prepared. Their physical properties and chemical behavior have been investigated.

2. It is shown that the reaction product from the condensation of acrolein and glycerol yields a five-membered acrylidene glycerol. The greater part of the reaction product is left as a thick, viscous residue. No indication was observed of the presence of the corresponding six-membered acetal, although it is possible that it may be formed and at once undergo spontaneous polymerization.

3. The corresponding acrylidene-glycerol methyl ether was prepared. It undergoes polymerization to a dimolecular form on standing.

4. The dihydroxypropylidene cyclic acetals of glycol and glycerol were prepared and their properties studied. They are apparently the first cyclic acetals of glycol and glycerol that have been prepared containing hydroxyl groups in the alkylidene radical.

5. Dihydroxypropylidene glycol and glycerol as well as dihydroxypropylidene-glycerol-α-methyl ether show no tendency to polymerize, a fact of some interest in connection with their relationship to cellulose and other polysaccharides.

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