MECHANISM
OF
CYCLIC ACETAL FORMATION

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A Thesis

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By

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MECHANISM OF CYCLIC ACETAL FORMATION.

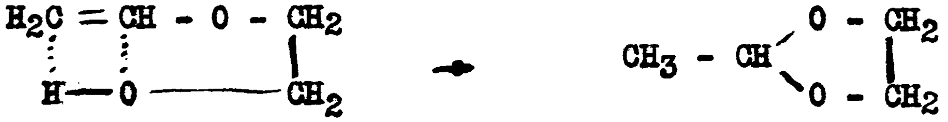
The importance of the cyclic acetals in relation to the chemistry of the carbohydrates is well recognized and their synthesis has been the subject of much experiment and study.1)

In earlier work2) dealing with the formation of cyclic acetals by the action of acetylene on polyhydroxy compounds in the presence of a catalyst, an interesting speculation as to the mechanism of this reaction was brought forward. With acetylene and ethylene glycol, for example, it was assumed that the first change involves the addition of one hydroxyl to the unsaturated acetylene linkage with formation of the intermediate hydroxy-ethyl vinyl ether, (A).

$$\overset{HC \equiv CH}{H - O} - CH_2 - CH_2OH \longrightarrow CH_2{=}CH - O - CH_2 - CH_2OH$$

(A)

and that (A), repeating the same general reaction, intra-molecularly rearranges as fast as formed into ethylidene glycol. (B).



(B)

The present investigation deals with the direct synthesis of the intermediate (A) and the establishment of its constitution. It is shown further that the rearrangement into (B), as indicated above, takes place in a most striking manner.

When pure, freshly prepared, hydroxy-ethyl vinyl ether is brought in contact with a trace of 40% sulphuric acid, an explosive reaction occurs, and the unsaturated alcohol-ether rearranges itself quantitatively into the saturated cyclic acetal, ethylidene glycol. Both the rate and the energy of this transformation are remarkable. In small amounts, however, and with strong cooling, the violence may be modified somewhat, although even under control the cyclization is complete within a very short time. Apparently almost any acid will affect this change in fact, traces of acetic acid formed by the slight hydrolysis and oxidation of the hydroxy-ethyl vinyl ether, caused by exposure to the air are sufficient to bring about rearrangement. It is difficult, therefore, to redistil the product without considerable molecular rearrangement taking place unless a trace of alkali has been added to remove all traces of acid. The unsaturated ether is quite stable towards alkalies in the cold.

A trace of very dry hydrogen bromide produces the same quantitative rearrangement and this, together with the fact that in no case could the presence of acetaldehyde be detected during, or after the change, would seem to preclude any chance that the reaction might be one of hydrolysis to vinyl alcohol and glycol, rearrangement of vinyl alcohol to acetaldehyde followed by normal acetal formation between the latter and the glycol. In this connection it should be noted that the benzoate of hydroxy-ethyl vinyl ether,

$$CH_2 : CH . O . CH_2 . CH_2 . O . CO . C_6H_5$$

prepared by the action of benzoyl chloride on (A) in dry pyridine solution shows no tendency to rearrange, or to react in any way with small amounts of acid, thus indicating a specific role of the hydroxyl group in this interesting transformation.

The quantitative nature of the rearrangement is proven not only by the recovery of over 90% of pure ethylidene glycol, but also by the fact that immediately after the reaction there is no indication of unsaturation when tested with a carbon tetra-chloride solution of bromine.

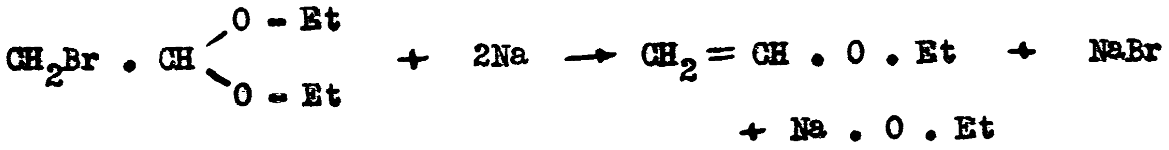
The identity of the ethylidene glycol was established beyond question by its analysis, boiling point, refractive index, solubilities, and its quantitative hydrolysis into acetaldehyde and ethylene glycol. It compared in every way with the product obtained from the reaction of acetylene, or acetaldehyde with ethylene glycol.2)

It is interesting to note the change of refractive index with rearrangement, it being 1.4565 for the unsaturated derivative (A) and 1.4037 for the isomeric cyclic acetal (B).

MECHANISM OF THE ACTION OF METALS ON HALOGENATED ACETALS

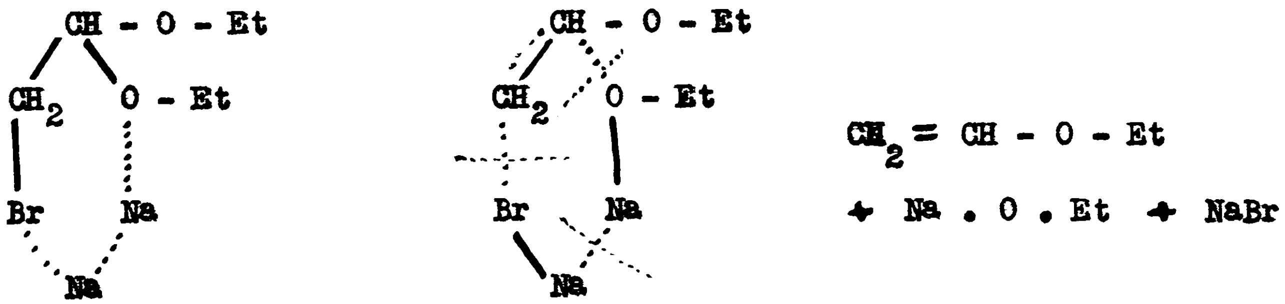
The vinyl glycol referred to above was obtained, as indicated in the experimental part, by the action of sodium on brom-ethylidene glycol and a discussion of this synthesis offers a number of points of considerable theoretical interest.

The reaction of this halogenated cyclic acetal with sodium might be expected to be analagous to that of brom-ethylal, which was investigated by Wislicenus[3] and was shown to proceed according to the equation:

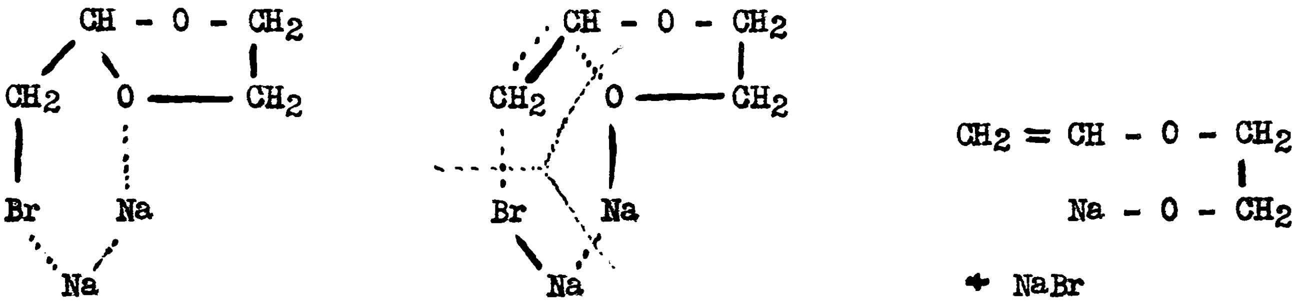


$$CH_2Br \cdot CH\begin{array}{l} ^{\diagup} O - Et \\ _{\diagdown} O - Et \end{array} + 2Na \longrightarrow CH_2 = CH \cdot O \cdot Et + NaBr + Na \cdot O \cdot Et$$

It was pointed out by Hibbert and Hill[1] that in the light of Erlenmeyer's theory of organic reactions,[4] this reaction may possibly take place through the formation of an unstable intermediate cyclic compound (C) with two sodium atoms followed by ring scission as indicated, graphically, below.



A similar reaction, therefore, with bromethylidene glycol might be expected to yield the sodium salt of Hydroxy-ethyl vinyl ether (D) and this is found to be the case.



When metallic sodium is added to a dry ether solution of this brom-cyclic acetal, a smooth but vigorous reaction takes place accompanied by a gradual separation of sodium bromide and the sodium salt of the unsaturated derivative (D). The latter compound is obtained in the free state, in 60% yield, by addition of water as described in the experimental part.

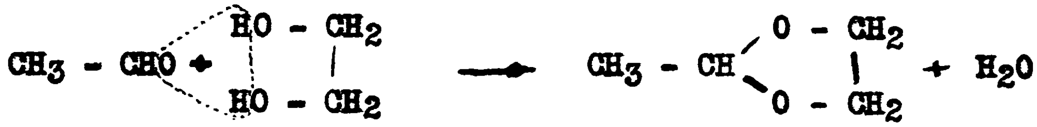
Hydroxy-ethyl vinyl ether is a colorless oil B.P. 45°/10 mm. and 140°/760 mm. soluble in water, alcohol, ether, and benzene, but insoluble in cold ligroin. It adds on bromine readily and the presence of a free hydroxyl group is shown by the evolution of hydrogen on treatment with sodium and also by the formation of a mono-benzoate, B.P. 133°/9 mm., by the action of benzoyl chloride in dry pyridine solution. Heating with dilute acids results in the formation of acetaldehyde and glycol.

In view of the high yield of hydroxy-ethyl vinyl ether obtained by the action of sodium on brom-ethylidene glycol, it would appear that such products show very little tendency to undergo the Würtz synthesis involving a linking up of the radicals after the manner characteristic of the hydrocarbons. If this method of synthesis had been applicable to these compounds it would have offered a convenient method of preparing compounds closely related in structure to the polysaccharides.

and attempts to accomplish this have been made previously 1) on the basis that the cyclic acetal grouping, being more stable than the open chain form, would not be attacked by the metal.

APPLICATION OF THEORY OF CYCLIC ACETAL FORMATION TO OTHER REACTIONS

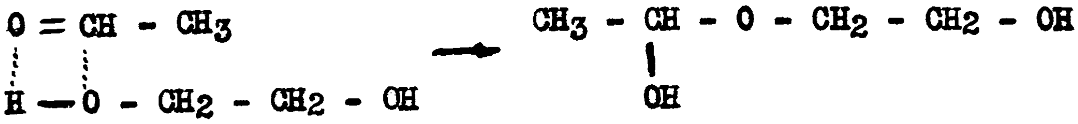
There would seem to be considerable significance in the instantaneous rearrangement of hydroxy-ethyl vinyl ether into ethylidene glycol, especially in view of the marked ease with which it takes place. Involving, as it does, the addition of an hydroxyl to a double bond, it suggests the possibility that formation of an intermediate unsaturated derivative may precede many of the reactions of hydroxyl compounds. Thus, for example, the cyclic acetal formation from acetaldehyde and glycol usually expressed by the equation:



$$CH_3-CHO+\begin{array}{l}HO-CH_2\\ \quad\ \ |\\ HO-CH_2\end{array}\longrightarrow CH_3-CH\begin{array}{l}\diagup O-CH_2\\ \qquad\ \ |\\ \diagdown O-CH_2\end{array}+H_2O$$

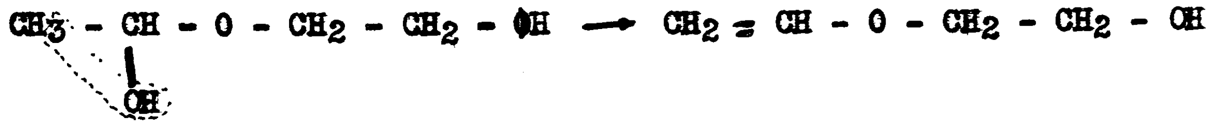
may, in reality consist of three consecutive reactions:

I. Addition of one of the hydroxyl groups to the carbonyl radical:



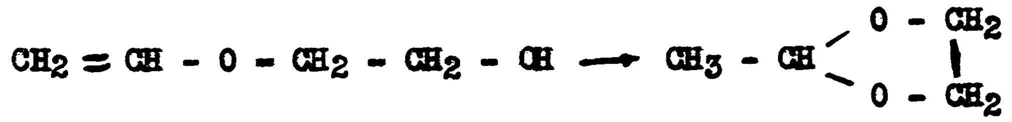
$$\begin{array}{l}O=CH-CH_3\\ \vdots\quad\ \vdots\\ H-O-CH_2-CH_2-OH\end{array}\longrightarrow \begin{array}{l}CH_3-CH-O-CH_2-CH_2-OH\\ \qquad\ \ |\\ \qquad\ OH\end{array}$$

II. Dehydration of the half acetal:



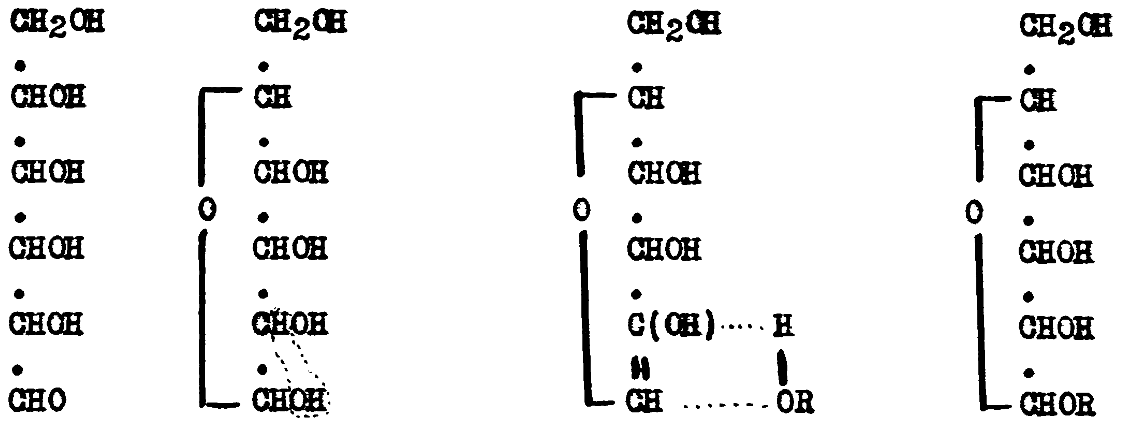
$$CH_3-\underset{OH}{CH}-O-CH_2-CH_2-OH \longrightarrow CH_2=CH-O-CH_2-CH_2-OH$$

III. Rearrangement as described in this paper:



With monohydric alcohols the scheme would be the same except that III would be an intermolecular, instead of intramolecular addition. Substituting formaldehyde for acetaldehyde, the dehydration (II) would take place from the same rather than from adjacent carbons.

It is of still greater interest to apply this mechanism to the reactions of the carbohydrate and polysaccharide groups. Thus, in glucoside formation the mechanism may consist of three reactions; paralleling the above:

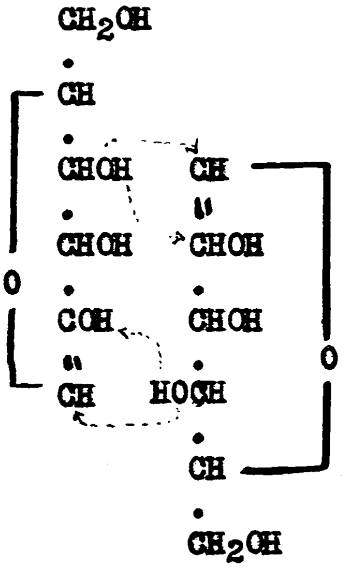


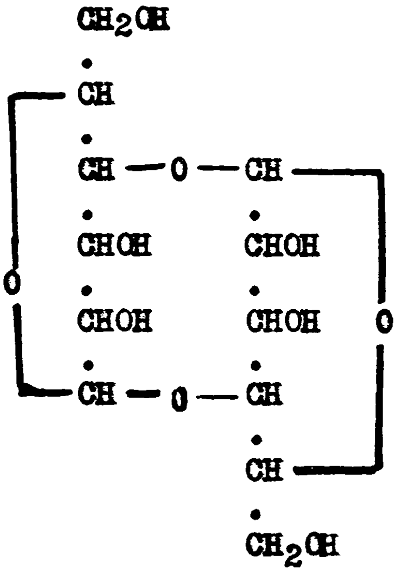
Here (I) is intramolecular and (III) is intermolecular.

If R is a second carbohydrate residue, a polysaccharide results.

It is to be noted that the unsaturated glucose derivative to which this reasoning leads is similar to glucal, discovered by Fischer[5] and further investigated by Bergman and his co-workers.

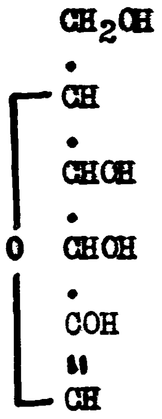
In the metabolism of the simple sugars into complex polysaccharides, the building-up process may proceed along the same lines, depending on the number of sugar residu~~c~~es present. In the case of cellulose, if it should be proven that there are two glucose residues linked in the cellulose nucleus, the scheme to form the biose anhydride starting with the unsaturated glucose derivative from stage (II) above, would be:

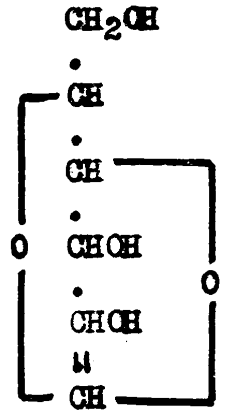




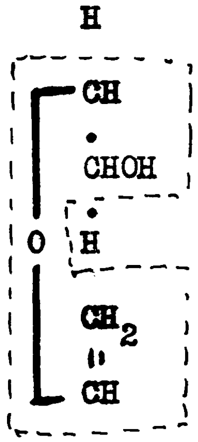
Here #4 hyrdoxyl adds on to the 1-2 unsaturation point of another similar molecule, the #4 hydroxyl of which adds in like manner to the double bond of the first.

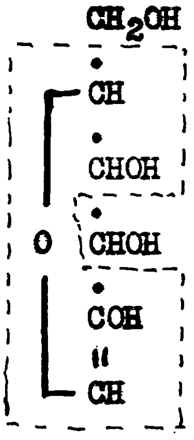
If, on the other hand, cellulose is a glucose anhydride it may be formed as above, except that #4 hydroxyl adds on to the unsaturated part of the <u>same</u> glucose derivative:





Incidentally this latter change involves the rearrangement of a hydroxyl and a double bond in the same relative positions as in the case of the hydroxy-ethyl vinyl ether described in this paper, each having analagous groups as marked out by the dotted lines:





The fact that the intermediate unsaturated sugar does not appear in these re-actions is no more surprising than that the prescence of the corresponding hydroxy-ethyl vinyl ether is not apparent in the preparation of the acetals from acetylene.

Dehydration between adjacent carbons, however, is a common property of all classes of polyhydroxy derivatives. This fact, coupled with the experimental evidence brought forward in this paper, leads towards the conclusion that among these unsaturated intermediate compounds may be found the key to the mechanism of many of the reactions of thos group, and that from their study some insight may be gained as to the nature of natural metabolism of the sugars and complex polysaccharides.

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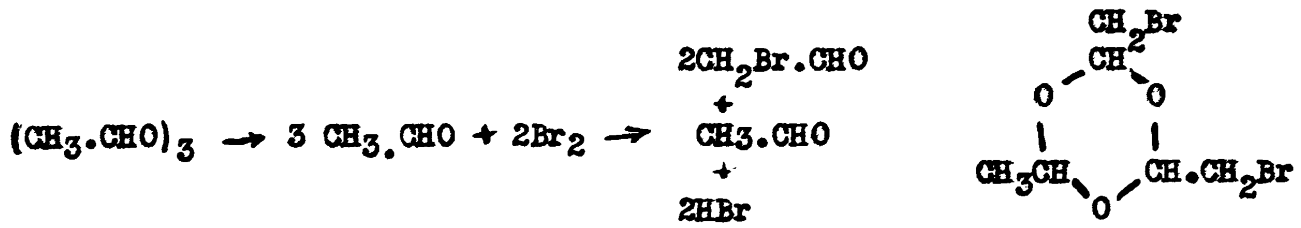
EXPERIMENTAL PART

Since the synthesis of the vinyl glycol ether (A) was accomplished by the action of metallic sodium on bromethylidene glycol, it was necessary to prepare the latter compound in quantity. Many experiments were carried out on the preparation of the bromacetal and more particularly of bromacetaldehyde which is the starting point for this and many other syntheses (1) in the field of carbohydrate chemistry.

BROMACETALDEHYDE

Direct bromination of paraldehyde at low temperatures yields a mixture of brominated paraldehydes of which the most easily isolated is di-brom paraldehyde. The early work in this field was done by Freundler and Ledru and others 6) although these workers did not obtain any definite products. Hibbert and Hill were the first to isolate bromacetaldehyde and tri-brom paraldehyde, although they generally employed a "crude extract" for their further syntheses[1]. Stepanow[7] by a more extended investigation of the conditions influencing this complicated reaction succeeded in improving the yield and in obtaining di-brom paraldehyde and mono-brom paraldehyde.

It appears that the bromination takes place on acetaldehyde; that is, the paraldehyde breaks down into acetaldehyde, which is then brominated and re-polymerizes to a brominated paraldehyde.



$$(CH_3.CHO)_3 \rightarrow 3\ CH_3.CHO + 2Br_2 \rightarrow \begin{array}{c} 2CH_2Br.CHO \\ + \\ CH_3.CHO \\ + \\ 2HBr \end{array}$$

The effect of temperature on this reaction is of supreme importance, if it is allowed to rise above 5°, two molecules of bromacetaldehyde "crotonize" under the influence of the high concentration of HBr.

$$2CH_2Br.CHO \longrightarrow CH_2Br.CH{=}CBr.CHO$$

The excess bromine at once enters the double bond to form tetra-brom butyraldehyde, yields of 80% have been recorded. The temperature must be kept low to retard this undesirable side-reaction, yet not so low as to make the bromination too slow.

The most critical stage of the reaction is the re-polymerization, this does not take place in the strong HBr solution even on standing for several days at temperatures below the crotonization point.

Unless the greater part of the free HBr is removed it is impossible to extract the stable product.

Hibbert and Hill, followed by Stepanow, used anaqueous sludge of crystalline sodium acetate which reduces the concentration of HBr, and seems to be a suitable medium for polymerization. Stepanow allowed two days for this polymerization to take place . In the present work, after many modifications of the above method were tried it was found possible to bring about the repolymerization by the addition of water, carefully keeping the temperature from rising during the addition. The HBr is removed from the reaction mixture by the water and the product solidifies. Yields up to 75% have been obtained by this method.

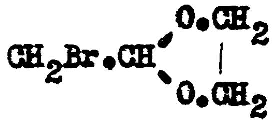
Details of Experiment.

105 grs. of freshly distilled paraldehyde are placed in a round bottom, three-necked flask, equipped with a dropping funnel, thermometer and mechanical stirrer. The contents of the flask are protected from moisture by a $CaCl_2$ tube, and a mercury seal. The flask is immersed in a freezing bath of ice and salt and 300 grs. of bromine. (dried in conc. H_2SO_4 and distilled) are slowly dropped into the well-stirred paraldehyde. The addition requires about five hours, the temperature during this time is maintained at -15°C. It is advisable to keep the mixture stirred for an hour or two after the addition of the bromine is completed as a precaution against local heating. The mixture is allowed to stand over night at temperatures ranging from -20° to -10°. Small pieces of ice are now slowly added during constant

stirring. The temperature during this addition is kept at -10°. This process is continued until the mass goes solid. The strong HBr solution is decanted off and the solid washed with water several times. The solid di-brom paraldehyde is placed in a large mortar and ground with carbonate and water to neutralize traces of HBr. It is filtered and washed with water. The yield of the crude product is 75% of theory. The white powder may be purified by crystallization from 90% alcohol to which a little KOH has been added to endure complete removal of acid. (If the alcholic solution becomes acid some of the product is lost due to acetal formation).

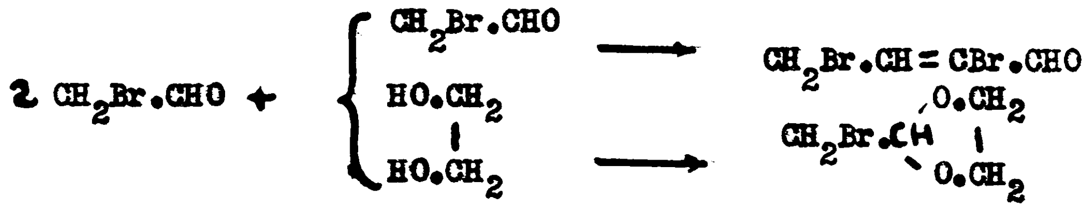
One mechanical difficulty to be overcome is the solidification of the paraldehyde when it is first placed in the cold flask. This renders the stirrer useless until the bromine has dissolved the paraldehyde. Local heating is inevitable and unstable side products are formed which tend to cause decomposition of the product. Attempts were made to obviate this by grinding the solidified paraldehyde and using a slow-moving sweeping stirrer. In this way the reaction mixture was kept homogeneous until the liquid stage was reached. Whether this method justified itself in yield or purity of final product was not definitely established. Iodine was tried as a catalyst, but no improvement in yeild could be detected. The rate of addition of bromine is very important, since too rapid addition may cause an explosion. It was found convenient to employ a dropping funnel with a visible dropper just below the tap.

PREPARATION OF BROM ETHYLIDENE GLYCOL FROM PARALDEHYDE.



$$CH_2Br.CH\begin{matrix}O.CH_2\\ |\\ O.CH_2\end{matrix}$$

By an application to this synthesis of certain knowledge gained during the work on the bromination of paraldehyde, yields have been considerably improved. The method developed by Hibbert and Hill[1] consists of bromination of paraldehyde followed by direct addition to the reaction flask of the appropriate polyhydric alcohol. This addition was made rather rapidly causing the temperature to rise in spite of the cooling bath. Since a rise in termperature favours the crotonization reaction there would be a partition of the aldehyde between crotonization and acetal formation:



$$2\ CH_2Br.CHO + \begin{cases} CH_2Br.CHO \longrightarrow CH_2Br.CH{=}CBr.CHO \\ \begin{matrix}HO.CH_2\\ |\\ HO.CH_2\end{matrix} \longrightarrow CH_2Br.CH\begin{matrix}O.CH_2\\ |\\ O.CH_2\end{matrix}\end{cases}$$

the amount of each formed depending on the relative speeds of reaction. An any case there is a considerable loss of the desired product. Since the undesirable crotonization is infinitely slow below 0^o, it may be completely prevented by keeping the temperature at -10^o during the addition of the alcohol and allowing longer time for the acetal formation to go to completion. Yields of 80% are obtained compared with 30 - 40% as prevoiusly recorded.

Details of experiment.

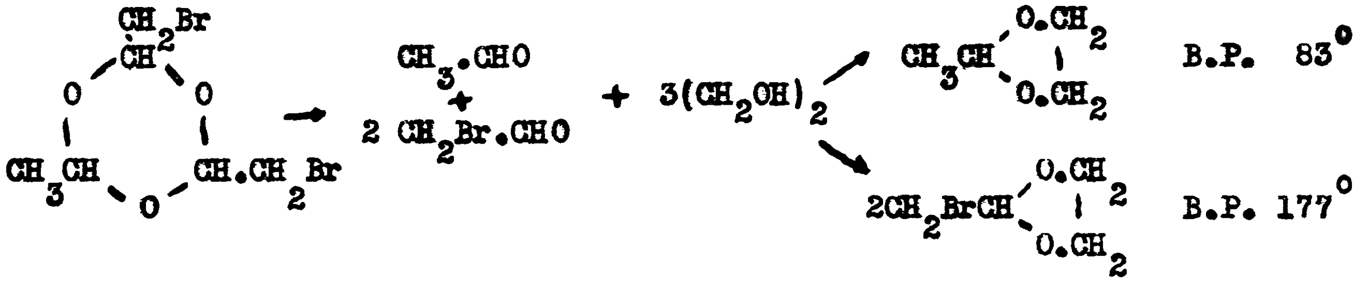
The flask was arranged as for the bromination of paraldehyde, a special stirrer being used, designed to obtain the maximum agitation of the two liquid layers. 125 grs. of paraldehyde and 100 c.c. (315) grs. of bromine are used, the bromination being conducted exactly as described above. After standing over night at a low temperature-0°to -10°the mixture still possessed a reddish colour, indicating excess bromine. The latter is removed by passing a little gaseous SO_2 into the mixture with stirring.

135 grs. of freshly distilled ethylene glycol are then added, drop by drop, the temperature being maintained at -10°. This addition requires about two hours and when it is completed the cooling bath is removedm the mixture allowed to attain to room temperature, and then is well stirred for six hours. It is now extracted with ether, neutralized with sodium carbonate, washed successively with small amounts of concentrated sodium bisulphite solution, water, 10% sodium hydroxide solution, water, and then dried over anhydrous sodium sulphate. After removal of the ether, fractionation of the residue under reduced pressure yields 260 grs. of brom-ethylidene glycol, boiling between 68° and 71° at 15 mm. pressure. The yield obtained is 80% of theory, calculated on the basis that all the bromine was available as bromacetaldehyde.

The product obtained by this method shows a slight tendency to darken on standing. A product which has become dark may be purified by shaking with dilute NaOH solution, followed by distillation.

PREPARATION OF BROM-ETHYLIDENE GLYCOL FROM CRYSTALLINE DI-BROM PARALDEHYDE.

Using pure crystalline di-brom paraldehyde a very pure bromacetal was obtained which shows no signs of darkening on standing. The reaction involved is as follows:



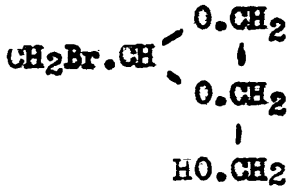
The two products may be separated by distillation.

Details of experiment.

In a flask equipped with a motor stirrer, mercury seal, and reflux condenser, 185 grs. of crystalline di-brom paraldehyde are placed. 140 grs. of ethylene glycol together with 30 drops of 40% sulphuric acid are addred. The mixture is stirred over a steam bath for ten hours. When the heating is commenced, the crystals melt (57°), and two liquid layers are formed, as the action proceeds the liquid becomes homogeneous and much more limpid. The reaction mixture is allowed to cool, extracted with either three times, and the extract treated exactly as described above for the product obtained direct from the bromination reaction flask.

After some of the low boiling fraction comes over, a very pure product distils, at 65°-66° under 12 mm. pressure. 77 grs. representing a yield of 40% are obtained. The poor yield is balanced in some measure by the extraordinary purity of the product, which may be distilled at atmospheric pressure without decomposition.

BROM ETHYLIDENE GLYCEROL



This compound was synthesized from crystalline di-brom paraldehyde by the method described above using an equivalent amount of glycerol in place of glycol. It is a viscous liquid boiling at 133°-134° at 12 mm.

ACTION OF METALLIC SODIUM ON BROM ETHYLIDENE GLYCOL.

Synthesis of Hydroxyl-ethyl vinyl ether

$$CH_2 = CH.O.CH_2.CH_2OH$$

Sodium reacts vigorously with the bromacetal in ether solution, but the heavy brown precipitate of sodium salts formed, soon brings the action to a stop and vigorous stirring and heating must be resorted to. The completeness of the reaction depends considerably on the power of the stirrer to continue expose fresh surfaces of metal. The action goes largely in one direction, but with an insufficient amount of sodium present the chance for side reaction is increased. It has not been found possible to obtain complete reaction of the theoretical amount of sodium.

Details of Experiment

Details of Experiment

75 grs. of brom-ethylidene glycol dissolved in three times the volume of anhydrous ether, are placed in a 500 c.c. flask. The flask is equipped with a motor stirrer, mercury sealm and reflux condenser, the end of which is appropriately protected against atmospheric moisture and CO_2. 20 grs. of metallic sodium are added in small pieces. A brisk reaction takes place causing the ether to boil, but after a time it subsides and gentle heat is applied. The heating and stirring are continued for seven hours. The ether now contains a heavy yellow suspension of sodium bromide and the sodium salt of hydroxy-ethyl vinyl ether, together with some unchanged sodium. As much as possible of this suspension is decanted from the sodium, fresh ether is added and the rest of the brown paste is washed from the metal in a manner similar to the gold panning process.

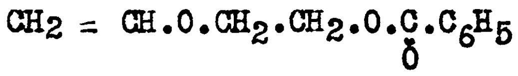
To the ether extract is added an amount of water just sufficient to dissolve the solid. The water layer is separated and extracted several times with ether. The ether extracts are combined and given one washing with a minimum amount of water to reduce the large excess of NaOH formed by the decomposition of the sodium salts. It is then dried over anhydrous sodium sulphate. After removal of the ether under a long bead column, the product is distilled under reduced pressure. The pure hydroxy-ethyl vinyl ether comes over between 44^0 and 45^0 under a pressure of 10 mm. A yield of 22 grs. is obtained correwponding to 56.4% of theory.

The product is a rather viscous liquid, possessing a pleasant ethereal odour and a refractive index of 1.4565. It is soluble in water, alcohol, ether benzene, and insoluble in cold ligroin, is strongly unsaturated, also shows the reactions characteristic of a hydroxyl group. It is free from halogen. Vinyl hydroxy-ethyl ether is very stable when distilled from a slightly alkaline medium, but in the presence of a trace of acid it reacts vigorously to form ethylidene glycol by intramolecular rearrangement.

Anal. Subs., .2105: CO_2, .4176; H_2O, .1729. Calc. for $C_4H_8O_2$ C. 54.54; H. 9.09. Found C. 54.15; H. 9.00

Attempts were made to ise magnesium activated with iodine according to the Bayer method. Magnesium does not react with brom ethylidene glycol in ether solution. If no solvent is employed the action is violent, beyond control, and decomposition takes place. Experiments were performed using toluene as a solvent, with little success. A small amount of a liquid was obtained which decomposed on heating, liberating iodine vapours, and indicating some compound formation with the iodine catalyst. In view of these difficulties the use of magnesium was abandoned in favour of sodium

PREPARATION OF THE BENZOATE OF HYDROXY-ETHYL VINYL ETHER



$CH_2 = CH.O.CH_2.CH_2.O.\underset{O}{C}.C_6H_5$

In order to identify further the product obtained by the action of sodium on brom-ethylidene glycol, the benzoate was prepared in the following manner:

10 grs. of hydroxy-ethyl vinyl ether is added slowly to a mixture of 10 c.c. of benzoyl chloride and 20 c.c. of pyridine (dried by refluxing over BaO). Considerable heat is evolved during the addition. The mixture is then poured into a large volume of water. An oil separates out, which is dissolved in ether. The water itself is extracted twice with ether. The combined ether extracts are washed with dilute NaOH solution, followed by water. The extract is then dries over anhydrous potassium carbonate. The ether is removed at ordinary pressure and the residue is distilled in vacuo. Traces of pyridine first distil are followed by the benzoate, B.P. 133° under a pressure of 9 mm.

The product so obtained is a slightly yellowish, viscous liquid , with an aromatic odour. It exhibits the high refractive index characteristic of benzoates. It reacts to an unsaturated derivative, but gives no vigorous reaction with acid, characteristic of the free alcohol

It is important to remove all traces of acid before distillation, or there is a tendency for decomposition to occur, resulting in more or less complete conversion of the benzoate into benzoic acid and other products. The acid thus formed soon prevents further distillation by subliming in to the delivery tube.

Anal. Subs. .2219; CO_2 .5406; H_2O .1108. Calcd. for $C_{11}H_{12}O_3$
C. 68.750; H. 6.25; Found. C. 68.755; H. 6.56

INTRAMOLECULAR REARRANGEMENT OF HYDROXY ETHYL VINYL ETHER TO ETHYLIDENE GLYCOL.

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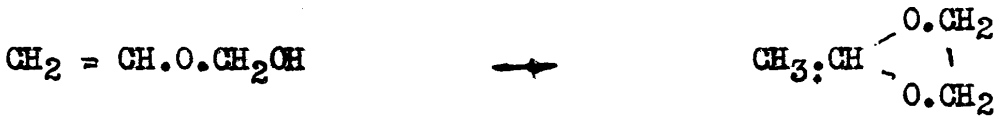

$$CH_2 = CH.O.CH_2OH \longrightarrow CH_3.CH\begin{array}{l}O.CH_2\\ \quad\;|\\ O.CH_2\end{array}$$

This change which is the final step in the mechanismof acetal formation takes place under the agency of a trace of acid. If the alcohol ether is very pure, the rearrangement is violent and can only be performed safely in test tube quantities. The following method was found practicable for the conversion of larger amounts of the alcohol:

2 c.cs. of hydroxy-ethyl vinyl ether are placed in a flask large enough to conveniently hold the final volume of the product to be converted. A drop of 40% sulphuric acid is added. When the reaction has stopped, fresh ether alcohol may be slowly added and, as it is converted as fast as added, the danger of explosion is obviated. Due to the great liberation of heat it is necessary to cool the flask to prevent loss of the ethylidene glycol.

The product formed has all the physical and chemical properties of ethylidene ethylene glycol. Refractive index, which previous to the reaction was 1.4565 is now 1.4035, which compares with a value of 1.4034 for ethylidene glycol prepared from acetylene and glycol.

In a quantative experiment 4.3 grs. of hydroxy-ethyl vinyl ether yielded 3.6 grs. of ethylidene glycol, thus approximating a 90% conversion.

Anal. Subs. .1404; CO_2 .3391; H_2O .1404. Calc. for $C_4H_8O_2$ C. 54.54; H. 9.09. Found. C. 54.09; H. 9.12

If the hydroxy-ethyl vinyl ether is impure this rearrangement will not take place explosively. Addition of acid causes spontaneous evolution of heat and in a minute or so the reaction is complete.

Other catalysts will bring about the same change. Dry HBr, concentrated sulphuric acid, and even traces of acetic acid, formed by slight hydrolysis and oxidation of the alcohol, will cause complete rearrangement,

QUANTATIVE HYDROLYSIS OF ETHYLIDENE GLYCOL OBTAINED BY INTRAMOLECULAR REARRANGEMENT OF HYDROXY-ETHYL VINYL ETHER.

To further confirm the identity of the product obtained above, it was hydrolyzed to acetaldehyde and glycol.

2.552 grs. of ethylidene glycol, together with 2 grs. of 5% phosphoric acid are placed in a test tube attached to a reflux condenser. From the top of the condenser a tube runs to a coil immersed in a freezing mixture. The coil was carefully weighed. Keeping the water in the condenser-jacket just above the boiling point of acetaldehyde the mixture was refluxed for one hour. The acetaldehyde collects in the coil and is weighed. 1.535 grs were obtained, corresponding to a conversion of 94% of the theoretical.

SUMMARY

1. Hydroxy-ethyl vinyl ether is readily synthesised by the action of metallic sodium on brom-ethylidene glycol.

2. Under the influence of a trace of acid this undergoes instantaneous, intramolecular rearrangement into ethylidene glycol.

3. This rearrangement is a strong argument in favour of the theory of hydroxy alkyl vinyl ether formation as an intermediate stage in the mechanism of cyclic acetal synthesis.

4. Halogenated cyclic acetals, such as brom-ethylidene glycol do not undergo the Wurtz synthesis under the influence of metallic sodium, but instead, yield hydroxy alkyl vinyl ethers.

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REFERENCES

1. Hibbert and Hill, J. Amer. Chem. Soc., 45, 734, (1923)
2. Hill and Hibbert, J. Amer. Chem. Soc., 45, 3108 (1923)
3. Wislicenus, Ann Ann., 192, 112 (1878)
4. Erlenmeyer, Ann., 316, 43 (1901)
5. (a) Fischer Ber., 47, 196 (1914)
   (b) Fischer, Bergmann, ahd Schotte, Ber., 53B, 509 (1920)
6. (a) Freundler and Ledru, Compt. Rend. 140, 794, 1693 (1905)
   (b) Freundler and Ledru, Bull. soc. chim. (4) 1, 66 (1907)
   (c) Burgorsky, Z. Physik. Chem., 48, 63 (1904)
   (d) Mauguin. Compt. rend. 147, 747 (1908)
7. Stepanow. Ber., 58, 1718 (1925)

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