might be reduced by 1000–3000 cal. at room temperature, making it approximately 28,000–30,000 cal. as compared to the above average of −34,200 cal., which also is for room temperature.

It is difficult to estimate the accuracy of our results. The most serious source of error is indicated by the presence of considerable amounts of methane among the products of some of the experiments. The corresponding side reaction undoubtedly has displaced equilibrium to some extent. However, in view of the facts that approximately the same end-point is reached from either side and that our calculated heat of reaction is not unreasonable, we are inclined to believe that our data are not greatly in error.

Summary

The position of equilibrium in the reaction $C_2H_6 \rightleftharpoons C_2H_4 + H_2$ has been measured at 600, 650 and 700°. Equilibrium was approached from both sides. Some uncertainty exists owing to the simultaneous formation of methane, but the indications are that the equilibrium constants at the three temperatures are 0.0310, 0.082 and 0.20, respectively, partial pressures being expressed in atmospheres.

PRINCETON, NEW JERSEY

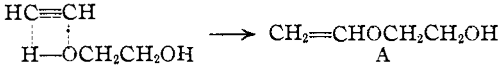
[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

THE MECHANISM OF THE ACETAL REACTION. THE EXPLOSIVE REARRANGEMENT OF HYDROXY-ETHYL VINYL ETHER INTO ETHYLIDENE GLYCOL[1]

HAROLD S. HILL[2] AND LLOYD M. PIDGEON

RECEIVED MAY 28, 1928 PUBLISHED OCTOBER 6, 1928

In a previous paper[3] dealing with the formation of cyclic acetals by the action of acetylene on polyhydroxy compounds in the presence of a catalyst, some speculations as to the mechanism of this interesting reaction were brought forward. Taking the reaction between ethylene glycol and acetylene as an example, it was assumed that the first change involves intermolecular addition of one glycol hydroxyl to the unsaturated acetylene carbons, giving hydroxy-ethyl vinyl ether, (A)



$$\begin{matrix} HC{\equiv}CH \\ \vdots \quad \vdots \\ H{-}OCH_2CH_2OH \end{matrix} \longrightarrow \underset{A}{CH_2{=}CHOCH_2CH_2OH}$$

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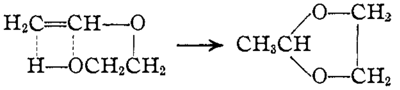
[1] This paper represents one of a series of publications carried out under the joint auspices of the Canadian Pulp and Paper Association, the Pulp and Paper Division of the Forest Products Laboratories of Canada and the Department of Industrial and Cellulose Chemistry, McGill University. The authors wish to express their appreciation of the facilities placed at their disposal by the three coöperating agencies.

[2] Research Fellow, Canadian Pulp and Paper Association.

[3] Hill and Hibbert, THIS JOURNAL, **45**, 3128 (1923).

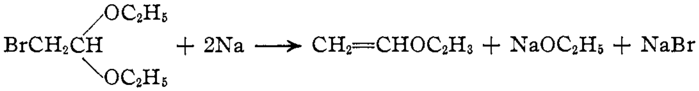
which, undergoing the same general reaction *intra* molecularly, rearranges at once to form ethylidene glycol.



B

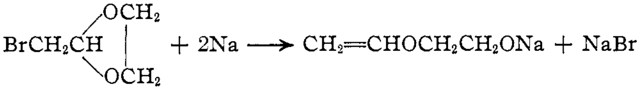
The present communication deals with the synthesis of the intermediate vinyl derivative (A) and shows that its rearrangement into the acetal (B) takes place in a most striking manner.

For the synthesis of hydroxy-ethyl vinyl ether recourse was had to a scheme proposed in an earlier paper.[4] Since Wislicenus[5] had obtained vinyl ethyl ether by the action of metallic sodium on bromo-ethylal, according to the equation



$$BrCH_2CH(OC_2H_5)_2 + 2Na \longrightarrow CH_2{=}CHOC_2H_3 + NaOC_2H_5 + NaBr$$

it was considered probable that a similar reaction with bromo-ethylidene glycol would yield the sodium salt of the desired intermediate (A)



and this is now found to be the case. When metallic sodium is added to a dry ether solution of bromo-ethylidene glycol, a smooth but vigorous reaction takes place accompanied by the gradual accumulation of sodium bromide and the sodium salt of hydroxy-ethyl vinyl ether. The latter compound is obtained by hydrolyzing the sodium salt with water and extraction as described in the experimental part.

Hydroxy-ethyl vinyl ether is a colorless oil, soluble in water, ether and benzene but insoluble in ligroin. It adds bromine readily at the double bond, and the presence of a free hydroxyl group is shown by the evolution of hydrogen on reaction with sodium and by the formation of a monobenzoate.

Rearrangement of Hydroxy-ethyl Vinyl Ether into Ethylidene Glycol.—When this vinyl derivative, freshly prepared as above, is brought in contact with a trace of 50% sulfuric acid, an explosive reaction takes place and the unsaturated ether rearranges quantitatively into cyclic ethylidene glycol. The violence and velocity of this transformation are remarkable. Using small amounts, however, and by strong cooling, it may be modified somewhat, although even under these conditions cyclization is complete within a very short time. Any strong acid suffices to effect this rapid change and less dissociated acids cause the same reaction but at a slower rate. In fact, heating hydroxy-ethyl vinyl ether

[4] Hibbert and Hill, This Journal, **45**, 740 (1923).

[5] Wislicenus, *Ann.*, **192**, 112 (1878).

alone in the air is sufficient to bring about gradual rearrangement as well as other changes. It is impossible, therefore, to redistil the vinyl derivative after it has been exposed to the air for any length of time. The reason for this may possibly be the formation of traces of acetic acid by slight hydrolysis and oxidation. Distillation is best carried out in the presence of a small amount of carbonate, or traces of sodium hydroxide. The product is quite stable in the presence of alkalies, although long boiling with dilute alkalies causes hydrolysis. The same change takes place with great ease in dilute acids, the products being acetaldehyde and ethylene glycol.

A trace of dry hydrogen bromide added to the vinyl derivative produces the same instantaneous rearrangement that was caused by concentrated sulfuric acid, which, together with the fact that in no case could the presence of free acetaldehyde be detected during or after the change, would seem to preclude the possibility that this transformation involves preliminary hydrolysis to vinyl alcohol, its rearrangement to acetaldehyde and the recombination of the latter product with ethylene glycol to give the cyclic acetal (B).

In this connection, it should be noted that the benzoate of hydroxyethyl vinyl ether, $CH_2{=}CHOCH_2CH_2{-}OCO{-}C_6H_5$, shows no tendency to rearrange or to react in any way in the presence of small amounts of acid, thus indicating a specific role of the hydroxyl group in this interesting transformation.

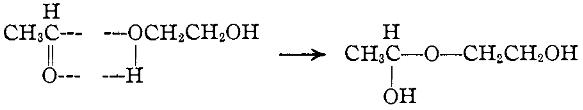
The quantitative nature of the rearrangement is proved not only in a recovery of over 90% of pure ethylidene glycol, but also by the fact that immediately after the reaction there is no trace of remaining unsaturation against bromine in carbon tetrachloride solution.

The identity of the ethylidene glycol formed was established beyond question by its 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 interaction of acetaldehyde (as paraldehyde) or of acetylene with ethylene glycol.

Theoretical Discussion

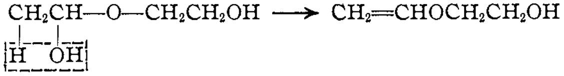
There would seem to be considerable theoretical significance attached to the above transformation, especially in view of the marked ease with which it takes place. Involving as it does the addition of a hydroxyl group to a *vinyl* double bond, it leads to the suggestion that intermediate unsaturation of this sort may precede many of the reactions of hydroxy compounds. Besides being the mechanism through which ethylene glycol reacts with acetylene, it may also serve as an explanation of acetal formation in general.

Thus, for example, the reaction of ethylene glycol with acetaldehyde may be represented as taking place in three stages: (1) addition of one glycol hydroxyl to the unsaturated C=O group to form a half acetal.[6]



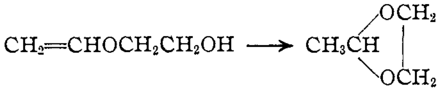
$$\begin{array}{ll} \overset{H}{CH_3C}\text{--} & \text{--}OCH_2CH_2OH \\ \| & | \\ O\text{--} & \text{--}H \end{array} \longrightarrow \begin{array}{c} H \\ CH_3C{-}O{-}CH_2CH_2OH \\ | \\ OH \end{array}$$

(2) dehydration



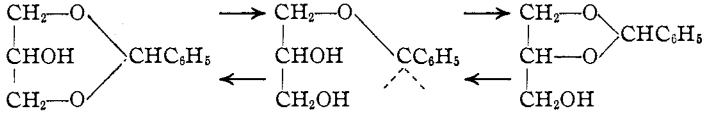
$$\underset{\boxed{H \quad OH}}{CH_2CH{-}O{-}CH_2CH_2OH} \longrightarrow CH_2{=}CHOCH_2CH_2OH$$

(3) rearrangement of the vinyl derivative as shown in this paper

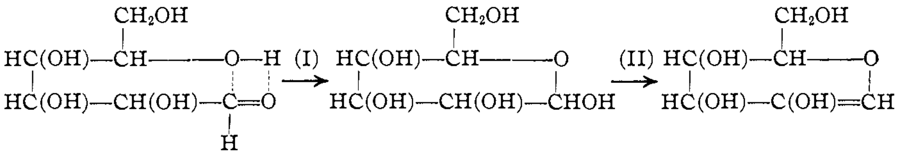


With monohydric alcohols instead of ethylene glycol, the scheme would be the same except that in the last stage the reaction would be intermolecular rather than intra molecular. Substituting formaldehyde or benzaldehyde for acetaldehyde, the dehydration in stage (2) would be from the same carbon. Such an unsaturated carbon compound has never been isolated, but there is much evidence that they occur as intermediates.

For example, it has recently been found[7] that a trace of dry hydrogen chloride causes the interconversion of 1,3-benzylidene glycerol to its 1,2-isomer and *vice versa*, a reaction probably taking place through an unsaturated intermediate



It is of special interest to apply this mechanism to reactions of the sugar and polysaccharide groups, in which the cyclic half acetal configuration is of such common occurrence. Thus, in glucoside formation, starting with the more unstable aldehydic form of glucose, the three identical stages of the acetal reaction above may occur.



$$\begin{array}{l} \qquad\quad CH_2OH \\ HC(OH){-}CH{-}{-}{-}O{-}H \\ HC(OH){-}CH(OH){-}C{=}O \\ \qquad\qquad\qquad\quad H \end{array} \xrightarrow{(I)} \begin{array}{l} \qquad\quad CH_2OH \\ HC(OH){-}CH{-}{-}{-}O \\ HC(OH){-}CH(OH){-}CHOH \end{array} \xrightarrow{(II)} \begin{array}{l} \qquad\quad CH_2OH \\ HC(OH){-}CH{-}{-}{-}O \\ HC(OH){-}C(OH){=}CH \end{array}$$

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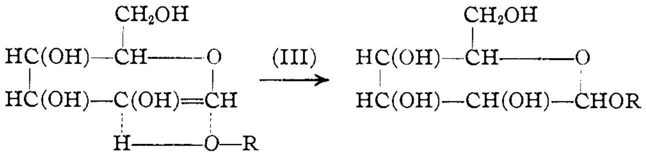
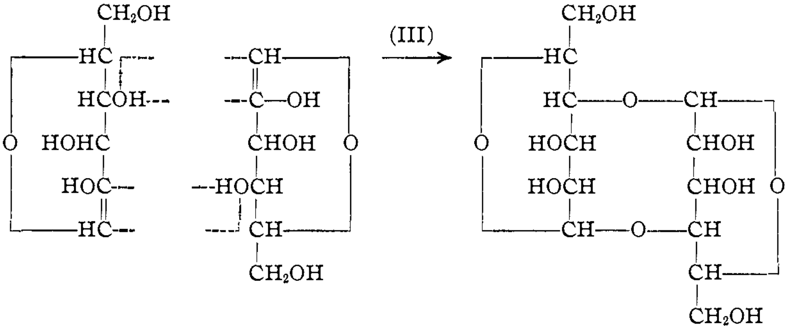
[6] Since this work was completed, Adkins and Broderick, THIS JOURNAL, **50**, 499 (1928), have brought forward evidence indicating that the formation of a half acetal, as in Equation 1 is, in fact, the first stage in the acetal reaction. From changes in refractive index it is shown that this initial addition takes place on merely bringing together a pure alcohol and an aldehyde.

[7] Hill, Whelen and Hibbert, THIS JOURNAL, **50**, 2238 (1928).



If (R) is another sugar residue, a polysaccharide results, and sugar metabolism in general may well proceed along these lines.

Assuming, for example, cellulose to be based on a unit of a biose anhydride, the latter might be formed from the -ene-1,2-glucose derivative (C) as follows



In like manner it is possible to interpret many other transformations of sugar derivatives.[8]

The fact that such an unsaturated sugar (C) does not appear in the course of these reactions is no more surprising than that the corresponding vinyl derivative is not apparent in the preparation of acetals from acetylene.

Dehydration between adjacent carbons, however, is a very commonly occurring reaction in many classes of hydroxy and polyhydroxy compounds. This fact, coupled with the experimental evidence brought forward above, leads to the conclusion that among these unsaturated vinyl

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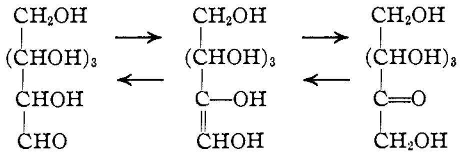
[8] Somewhat different unsaturated intermediates have been proposed as a basis for the explanation of certain transformations of sugar derivatives in *alkaline* solution. Thus Wohl, *Ber.*, **33**, 3095 (1900), postulated a scheme in which the glucose-mannose fructose interconversion takes place through an intermediate "enediol" form



Recent investigations of Evans and his co-workers have yielded much experimental evidence in favor of this mechanism, THIS JOURNAL, **47**, 3085, 3098, 3102 (1925); **48**, 2665, 2678, 2703 (1926); **50**, 486 (1928); see also Wolfrom and Lewis, *ibid.*, **50**, 837 (1928).

derivatives there may prove to be the key to the mechanism of many of the reactions of this group, including such important changes as occur in natural metabolism of sugars and polysaccharides.

Experimental Part

Preparation of Bromo-ethylidene Ethylene Glycol.[9]—One hundred and twenty-five g. of paraldehyde was brominated at $-12°$ as described[4,10] with 315 g. of bromine. After stirring the brominated mixture at $-10°$ for ten hours, a slight excess of bromine was removed by bubbling in sulfur dioxide with stirring. One hundred and thirty-five g. of ethylene glycol was added during two hours through a dropping funnel, keeping the temperature below $-10°$. The cooling bath was then removed and efficient stirring continued for six hours at room temperature. The mixture was extracted with ether, neutralized with sodium carbonate, washed successively with small amounts of concentrated sodium bisulfite solution, 10% sodium hydroxide, water and dried over solid potassium carbonate. After removal of the ether, fractionation under reduced pressure yielded 260 g. of bromo-ethylidene glycol, b. p. 68–71° (15 mm.). The yield is 80% of the theoretical calculated on the basis that all of the bromine was available as bromo-acetaldehyde.

The product obtained by this method shows a tendency to darken on standing. It may then be purified by shaking with 10% sodium hydroxide solution, followed by redistillation.

Bromo-ethylidene glycol may also be prepared by the interaction of ethylene glycol with crystalline dibromoparaldehyde[10] in the presence of 40% sulfuric acid as a catalyst.

One hundred and forty g. of ethylene glycol with 2 cc. of 40% sulfuric acid was added to 185 g. of dibromoparaldehyde (m. p. 57°) in a three-necked flask equipped with a stirrer, mercury seal and reflux condenser. The mixture was heated on the steam-bath with stirring for ten hours, after which it was worked up as in the above experiment. Fractionation gave some low boiling ethylidene glycol, followed by bromo-ethylidene glycol; b. p. 65–66° (12 mm.); yield, 77 g. or 40%. The yield is poor but the product is very pure and shows no darkening on standing.

Action of Metallic Sodium on Bromo-ethylidene Glycol. Preparation of Hydroxy-ethyl Vinyl Ether.—Seventy-five g. of bromo-ethylidene glycol dissolved in three volumes of anhydrous ether was placed in a 500cc. flask equipped with a motor stirrer, mercury seal and reflux condenser protected against atmospheric moisture and carbon dioxide. Twenty g. of clean metallic sodium was added in small pieces as rapidly as convenient. A brisk reaction took place, causing the ether to boil, but after a time this subsided and gentle heat was applied. Heating and stirring were continued for seven hours. It is well to have vigorous and efficient stirring in order to expose fresh surfaces of the sodium. The ether contained a heavy suspension of the sodium salt of hydroxy-ethyl vinyl ether, together with sodium bromide and some unchanged sodium. The latter was removed by flushing through a wire gauze with ether. The ether sludge so obtained was treated with an amount of water just sufficient to dissolve the solids, the first of this being added cautiously on the chance that bits of sodium might be present. The water layer was separated and extracted several times with ether. The ether extract was washed once with a minimum amount of water and dried over potassium carbonate. After removal of the ether, employing a column, the product was distilled under reduced pressure. Apparently the only product of the reaction was hydroxy

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[9] This product was isolated earlier (ref. 4) but by the above modifications the yield has been doubled.

[10] Stepanow, *Ber.*, **48**, 1718 (1925).

ethyl vinyl ether, b. p. 44–45° (10 mm.); 140° (760 mm.); yield 22 g., or 56.4% of the theoretical.

Anal. Subs., 0.2105: CO_2, 0.4176; H_2O, 0.1729. Calcd. for $C_4H_8O_2$: C, 54.54; H, 9.09. Found: C, 54.15, H, 9.00.

The product is a slightly viscous, colorless oil having a faint ethereal odor and n_D^{17} = 1.4564. It is soluble in water, alcohol, ether and benzene but insoluble in ligroin. It is strongly unsaturated against bromine in carbon tetrachloride, and against potassium permanganate, and also shows the reactions characteristic of the hydroxyl group. This vinyl derivative is stable when distilled from a slightly alkaline solution but is very sensitive to acids, dilute acids causing hydrolysis and traces of concentrated acids bringing about intramolecular rearrangement.

Benzoate of Hydroxy-ethyl Vinyl Ether.—Ten grams of the vinyl derivative (freshly prepared) was benzoylated in the usual manner with 10 cc. of benzoyl chloride and 20 cc. of dry pyridine. Pouring the reaction product into water, extracting with ether, washing the ether solution with cold dilute sodium hydroxide followed by water, drying over potassium carbonate and fractionating gave the benzoate of hydroxy-ethyl vinyl ether, b. p. 133° (9 mm.)

Anal. Subs., 0.2219: CO_2, 0.5406; H_2O, 0.1108. Calcd. for $C_{11}H_{12}O_3$: C, 68.75; H, 6.25. Found: C, 68.75; H, 6.56.

The product is a viscous oil, reacting as an unsaturated derivative, but in contrast to the free alcohol above shows no activity in contact with a trace of concentrated acid.

Intramolecular Rearrangement of Hydroxy-ethyl Vinyl Ether into Ethylidene Glycol.—As already described, this reaction takes place under the agency of a trace of concentrated acid. If the vinyl derivative is freshly prepared and pure, the rearrangement is so violent that it can be carried out safely only in test-tube quantities. The following modification was found practicable for the conversion of larger amounts of the unsaturated ether.

Two cc. of hydroxy-ethyl vinyl ether was placed in a flask large enough to hold the final volume of the product to be converted. A fraction of a drop of 40% sulfuric acid was added with cooling. After the rapid reaction had taken place, fresh vinyl derivative was slowly added and, since it was converted progressively, the danger of too violent a reaction was obviated. Cooling was necessary to prevent loss of ethylidene glycol.

The product so formed had all the physical and chemical properties of ethylidene glycol, b. p. 81–82° (760 mm.); n_D^{17} = 1.4035, as compared with n_D^{17} = 1.4565 for the vinyl derivative before rearrangement; n_D^{17} of ethylidene glycol prepared from acetylene and glycol, 1.4034.

Anal. Subs., 0.1404: CO_2, 0.3391; H_2O, 0.1404. Calcd. for $C_4H_8O_2$: C, 54.54; H, 9.09. Found: C, 54.09; H, 9.12.

In a quantitative experiment 4.3 g. of hydroxy-ethyl vinyl ether yielded 3.5 g. of ethylidene glycol, b. p. 81–83° (760 mm.), approximating a 90% recovery.

To confirm further the identity of the ethylidene glycol obtained above, it was quantitatively hydrolyzed to acetaldehyde and glycol; 2.552 g. of the product together with 2 g. of 5% phosphoric acid was placed in a test-tube attached to a small reflux condenser maintained at 40–50°. Gases from the condenser were led through a strongly cooled trap. Boiling the mixture in the tube for one hour yielded 1.535 g. of acetaldehyde in the trap, which corresponds to a recovery of 94% of the theoretical amount to be obtained by the hydrolysis of ethylidene glycol.

Acknowledgment is made of the receipt by one of us (L. M. P.) of a grant from the National Research Council of Canada, during the tenure of which this work was performed.

Summary

1. The synthesis of hydroxy-ethyl vinyl ether is described.
2. It is shown that this vinyl derivative in contact with a trace of concentrated acid undergoes instantaneous rearrangement into ethylidene glycol.
3. The latter change is offered as strong support for a mechanism proposed for the acetal reaction postulating a "vinyl" derivative as an intermediate product.
4. This mechanism is elaborated so as to include similar reactions such as those occurring in glucoside and polysaccharide formation.

MONTREAL, CANADA

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

VINYL DERIVATIVES: THEIR RELATIONSHIP TO SUGARS AND POLYSACCHARIDES[1]

BY HAROLD S. HILL[2]

RECEIVED MAY 28, 1928 PUBLISHED OCTOBER 6, 1928

In a preceding[3] paper dealing with the mechanism of acetal formations, the synthesis of hydroxy-ethyl vinyl ether and its rearrangement into ethylidene glycol are described. The extreme ease and the instantaneous character of the latter change led to the suggestion that unsaturated derivatives of the vinyl type may be the intermediates through which many other reactions of hydroxy compounds take place. From the application of this idea to the transformation of the sugars and polysaccharides, it was concluded that an unsaturated sugar[4] such as (IV) which may be considered as a vinyl derivative occupies a position of importance in a logical scheme picturing the mechanism of such reactions as occur in glucoside and polysaccharide formation.

The present paper describes the synthesis of additional vinyl derivatives, their transformations, and shows that the relationship indicated above is in fact a close one.

It seemed desirable first of all to show that the rearrangement of hydroxy-ethyl vinyl ether into ethylidene glycol

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[1] This paper represents one of a series of publications carried out under the joint auspices of the Canadian Pulp and Paper Association, the Pulp and Paper Division of the Forest Products Laboratories of Canada and the Department of Industrial and Cellulose Chemistry, McGill University. The author wishes to express his appreciation of the facilities placed at his disposal by the three coöperating agencies.

[2] Research Fellow, Canadian Pulp and Paper Association.

[3] Hill and Pidgeon, THIS JOURNAL, **50**, 2718 (1928).

[4] This unsaturated sugar is somewhat similar to Fischer's glucal, *Ber.*, **47**, 196 (1914) and also to the enolic form of glucose postulated by Wohl, *Ber.*, **33**, 3095 (1900), as an intermediate in the glucose-mannose-fructose interconversion.