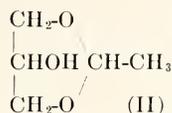
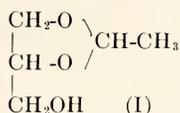


THE FORMULA OF ETHYLIDENE GLYCEROL.

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Ethylidene glycerol is capable of existence in two isomeric forms. Because of their similarity in properties and their instability, no evidence was brought forward to show which of the following formulas should be considered as correct.



Hill and Hibbert¹ showed from partition experiments that both forms must be present in ethylidene glycerol made by either the acetylene or the acetaldehyde method of preparation.

Recent work by Hill, Hill, and Hibbert² has shown that glycerol acetal made from paraldehyde consists of 80 per cent (I) and 20 per cent (II), and that from the acetylene method (mercuric sulfate and sulfuric acid catalyst) is 64 per cent (I) and 36 per cent (II). Separation and identification of the isomers was made possible by benzoylation in pyridine and separation of the benzoates in cold ligroin.

Using as catalysts mercuric oxide and anhydrous fluo-acids, the authors have prepared ethylidene glycerol, as well as other cyclic acetals, from acetylene.

In our procedure care is taken not to allow the liquid to become hot, the maximum temperature being 37°C. Because of this and because we use a less strongly acid catalyst, our product contains less low-boiling material. This indicates a predominance of the 1-2 acetal (I).

Methylation of the acetal by adding sodium and treating with methyl sulfate gave a 76 per cent yield of the methyl ether, b.p. 145-151°C., d_4^{25} 1.0135, n_D 1.4155. This is identical with the product formed from glycerol α -methyl ether and acetylene, b.p. 145-147°C., d_4^{25} 1.0098, n_D 1.4145. This shows that the 1-2 compound is present in large quantity or that it is considerably more reactive than its isomer. Similar, but less certain evidence was obtained from the acetal of glycerol α -chlorhydrin.

From these evidences and from a comparison of the properties of our compounds with the pure isomers made by Hill, Hill and Hibbert,² we concluded that our product was in large proportion the 1-2 acetal (I).

TABLE I. INDICES OF REFRACTION.

| | |
|---|--------|
| 1-3 Ethylidene glycerol ² | 1.4532 |
| 1-2 Ethylidene glycerol ² | 1.4413 |
| "Ethylidene glycerol" ³ | 1.4395 |
| 1-3 Ethylidene glycerol methyl ether ² | 1.4375 |
| 1-2 Ethylidene glycerol methyl ether ² | 1.4177 |
| "Ethylidene glycerol methyl ether" ³ | 1.4155 |

¹ Hill and Hibbert, *J. Am. Chem. Soc.*, 45, 3121, (1923).

² Hill, Hill, and Hibbert, *ibid.*, 50, 2242, (1928).

³ As prepared by the authors.

"*Proc. Ind. Acad. Sci.*, vol. 38, 1928 (1929)."

In order to check this, we benzoylated 39 g. of our product and separated the isomers. We obtained 5 g. of the crystalline benzoate (from 1-3 ethylidene glycerol) m.p. 86°C, and 18 g. of the liquid benzoate (from 1-2 ethylidene glycerol), b.p. 163°C. 11 mm. The ratio of the two isomers is then 1:3.6 or our product consists of 78 per cent 1-2 ethylidene glycerol (I) and 22 per cent 1-3 ethylidene glycerol (II).

Formation of (I) is thus shown to be favored by the use of fluo-acid catalyst and by keeping the liquid cool during the reaction.

CUPROUS CHLORIDE AS A CATALYST FOR ACETYLENE.

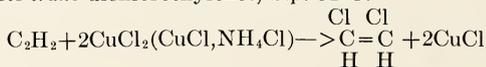
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Neutral or acid solutions of cuprous chloride and alkali chlorides or ammonium chloride absorb acetylene, forming several derivatives according to conditions. Intermediate products are probably formed, the final products being given off when the mixture is heated.

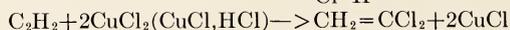
When cuprous and ammonium chlorides are used in solution saturated with hydrogen chloride gas, vinyl chloride is formed in about 30 per cent yield. The addition of an organic solvent is necessary to keep the very volatile vinyl chloride in solution.



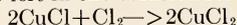
A mixture of cupric, cuprous and ammonium chlorides acts as a chlorinating agent. Acetylene passed into this solution forms the equilibrium mixture of *cis* and *cis-trans* dichlorethylenes, b.p. 54°C.



Cuprous and cupric chlorides, with or without ammonium chloride saturated with hydrochloric acid, give on treatment with acetylene a mixture of unsymmetrical and *cis-trans* dichlorethylenes. This is interesting as being the only synthesis which gives one of the symmetrical compounds without the other, also in that an unsymmetrical chlorination product is formed from a symmetrical hydrocarbon. The unsymmetrical dichlorethylene is identified by its boiling point (37°C.) and from its forming chloracetyl chloride and a solid polymerized product on standing in contact with air. The *cis-trans* compound is identified by its boiling point (48°C.). The *cis* isomer, b.p. 60°C., is not present.



After the products have been removed by heating, cupric chloride is regenerated by passing chlorine into the solution. Some cuprous chloride must be left in the solution for catalysis.



Solutions of cupric chloride in the absence of cuprous chloride do not absorb acetylene.

The mechanism of these reactions is unknown and will probably remain so until the constitution of chlorocupric acid (HCuCl_3 or $\text{CuCl}_2 \cdot \text{HCl}$) and chlorocuprous acid (H_2CuCl_3 or $\text{CuCl} \cdot 2\text{HCl}$) is more fully understood.