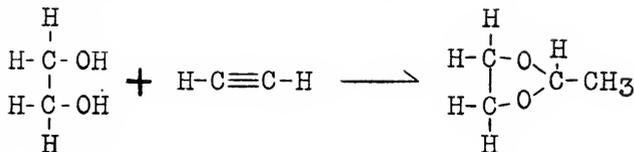


## THE CATALYTIC SYNTHESIS OF GLYCOL ACETAL

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In 1930 Nieuwland, Vogt and Foohey<sup>1</sup> reported that in the presence of mercuric oxide and boron fluoride ethylene glycol and acetylene condense to form glycol acetal in accordance with the following equation.



Glycol acetal has been known since 1861 when it was prepared by Wurtz<sup>2</sup> by the heating of acetaldehyde and paraldehyde with ethylene glycol. It was later shown that the material could be obtained in better yield by the addition of dehydrating agents to the reaction mixture<sup>3</sup>. Hill and Hibbert<sup>4</sup> prepared the material from acetylene using mercuric sulfate and sulfuric acid as catalysts. The method advanced by Nieuwland, Vogt and Foohey<sup>1</sup> has several advantages over the older methods and can be generally applied to hydroxy compounds.

The purpose of this article is to present an improved experimental procedure for the catalytic preparation of glycol acetal. By the use of this improved procedure a ten per cent higher yield and a purer product can be obtained than previously reported. In addition to these advantages the absorption of acetylene consumes less time and requires practically no attention.

## MATERIALS

Acetylene was obtained from a 40 cu. ft., Prestolite cylinder and was purified as described in the procedure. Ethylene glycol was obtained from the Eastman Kodak Company and boiled at 198-200°C. The mercuric oxide was of the red variety and was a standard C.P. grade.

Boron fluoride was prepared by the action of sulfuric acid on a mixture of boron trioxide and calcium fluoride. Two hundred grams of finely powdered boron trioxide was intimately mixed with 400 g. of calcium fluoride in a 3-l. Erlenmeyer flask. Thirteen hundred milliliters of concentrated sulfuric acid was added, and the mixture well shaken. Some silicon fluoride which was formed when the acid was added was allowed to escape. The mixture was heated with a small Bunsen flame and the boron fluoride evolved, passed through concentrated sulfuric acid

<sup>1</sup> Nieuwland, Vogt and Foohey, *J. Am. Chem. Soc.*, **52**:1018-24 (1930).

<sup>2</sup> Wurtz, *Compt. rend.*, **53**:378 (1861). *Ann.*, **120**:328 (1861).

<sup>3</sup> Tochert, *Ann. chim. phys.*, (6) **16**, 26, (1889); Clarke *J. Chem. Soc.*, **101**, 1803 (1912).

<sup>4</sup> Hill and Hibbert, *J. Am. Chem. Soc.*, **45**:3113 (1923).

"*Proc. Ind. Acad. Sci.*, vol. 42, 1932 (1933)."

and into methyl alcohol. The absorption flask was kept at 20-5°C. by cooling with ice water. If the heating should be interrupted for any reason, the generator must be vigorously shaken before heating is resumed, in order to break up the cake of calcium sulfate which forms.

#### PROCEDURE

In a three-necked, 2-1, tarred flask, fitted with an inlet tube, a mercury sealed Benning's stirrer<sup>1</sup>, and an outlet tube connected to a rubber bladder and a mercury manometer equipped with contacts for closing a bell circuit (Figure 1), is placed 10 g. of a 55-65 per cent solution

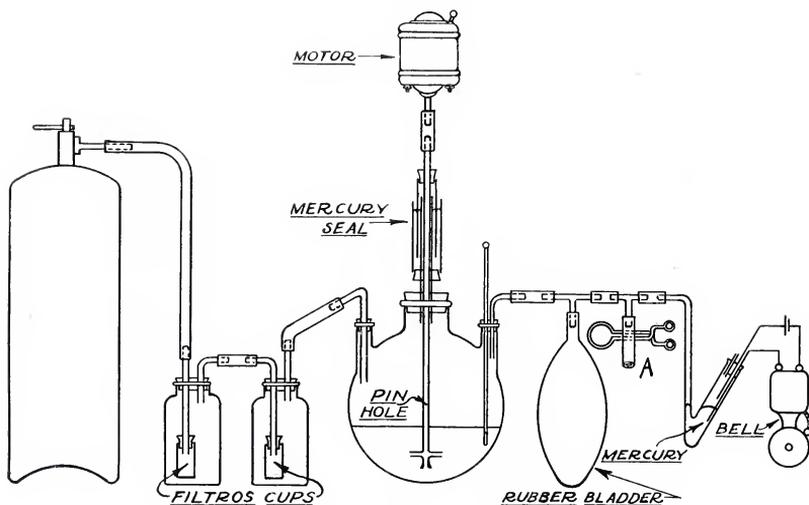


Fig. 1.

of boron fluoride in methyl alcohol, and 4 g. of mercuric oxide. The flask is allowed to stand two minutes until the mercuric oxide is partially dissolved and 248 g. (4 moles) of ethylene glycol added. Acetylene, from a Prestolite cylinder, is washed with water to remove acetone, dried with concentrated sulfuric acid (Note 1) and passed into the flask through the inlet tube. The pinch cock A is opened and the air completely displaced by acetylene. The pinch cock is closed and the stirrer started. The acetylene is rapidly absorbed (Note 2) and there is a considerable evolution of heat. The flask is kept cool (30-50°C.) by immersing it in ice water.

The stirring is continued about three hours, until 100-104 g. (4 moles) of acetylene has been absorbed (Note 3) and the flask is disconnected. The mercury sludge is allowed to settle (Note 4) and the liquid decanted into a separatory funnel. The acetal is washed twice with 100 cc. portions of a 50 per cent solution of potassium carbonate (Note 5) and dried over calcium chloride for two hours. The dried acetal is fractionated through a 3 ft. Vigreux column. The fraction

<sup>1</sup> Benning, Proc. Ind. Acad. Sci., 37:263 (1927).

boiling at 80-3°C. is collected. The yield of glycol acetal is 240-60 g. (67-73 per cent of the theoretical amount based on the acetylene absorbed).

Acetals of other glycols can be prepared by this method.

#### NOTES ON PROCEDURE

1. Complete drying is necessary to prevent the formation of acet-aldehyde and consequent tarring of the reaction mixture. This can be readily accomplished by spraying the wet gas through a Filtros cup into concentrated sulfuric acid as shown in Figure 1. If desired the water wash may be omitted as the sulfuric acid removes most of the acetone.

2. During the reaction the stream of acetylene is easily regulated by observing the rubber bladder, which should be partially inflated. If this is increasing in size the flow of gas should be diminished and, if decreasing, the flow should be increased. Should the pressure in the flask increase above 4-5 cm. of mercury (contacts should be set for this pressure) the bell rings and calls attention to the fact. Should the warning be ignored the excess acetylene bubbles through the mercury.

3. It is sometimes necessary to add 4 g. portions of mercuric oxide to replace that destroyed by the action of the acetylene. Marked slowing of the reaction indicates that the catalyst is spent.

4. The flask should be tilted as far to one side as possible during the settling in order that the clear liquid can be poured off the sludge without disturbing it. If necessary the contents of the flask should be filtered through cotton.

5. After shaking with the first portion of potassium carbonate solution the lower layer is cloudy due to the presence of insoluble inorganic fluo compounds. Only about two thirds of this should be run out as it is sometimes almost impossible to sharply separate the layers. On addition of the second portion of wash solution the remaining fluo-borates dissolve.

#### SUMMARY

An improved procedure for the synthesis of glycol acetal from acetylene and glycol has been described. By the use of this procedure a 67-73 per cent yield of the pure acetal may be obtained. The procedure requires less time and attention than any previously described.

