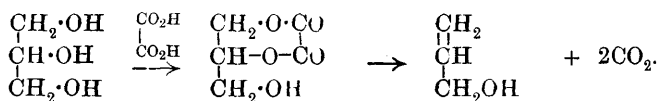


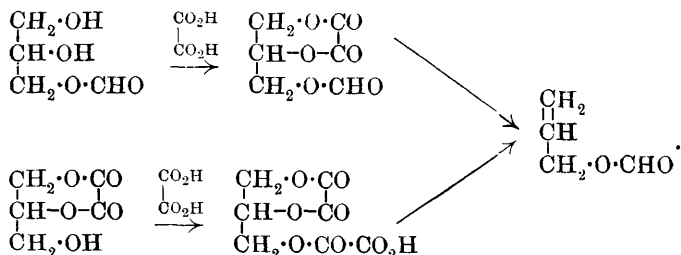
XLVII.—*The Preparation of Allyl Alcohol.*

By FREDERICK DANIEL CHATTAWAY.

ALLYL alcohol was first prepared from allyl iodide. This, however, since it had to be made from glycerol, was usually mixed with *isopropyl iodide*, from which it could be separated only with difficulty. The various procedures adopted to replace the iodine by hydroxyl were, moreover, somewhat complicated, and the yields consequently poor. These older methods were therefore at once abandoned when Tollens discovered that allyl alcohol could be obtained directly from glycerol by heating it with oxalic acid. It has recently been shown (T., 1914, **105**, 151) that allyl alcohol is produced in this reaction by the decomposition at a high temperature of the normal oxalic ester of glycerol, namely, dioxalin, which is one of the first products of the interaction of oxalic acid and glycerol:



Allyl formate, which is always obtained together with the allyl alcohol and gives to the crude product its extraordinarily irritant quality, results from a similar decomposition of monoformindioxalin, which may be produced either from monoformin by the further action of oxalic acid or from dioxalin by the formation and decomposition of an acid oxalate, both actions probably occurring:



This elucidation of the course of the reaction shows that the most favourable conditions for the production of allyl alcohol are those which promote the formation of the normal dioxalins, and that any are disadvantageous which tend to their hydrolysis. It is best, therefore, to work with anhydrous materials, as thereby the

dioxalins are formed in the largest possible amount, and the production of the acid oxalate, which, by its decomposition, yields monoformin, is as far as possible prevented.

It is advantageous also to use a considerable excess of oxalic acid, the allyl formate, which is in consequence obtained in larger amount, being easily hydrolysed to the alcohol if not required.

The following procedure has been found most speedy and advantageous. It gives a theoretical yield of allyl alcohol from the glycerol actually reacting, and even when the amount of oxalic acid used is considered gives a yield twice as great as the best that can be obtained by Tollens and Henninger's familiar method.

Five hundred grams of anhydrous oxalic acid are added to 500 grams of glycerol in a 1.5 litre flask, and the mixture is heated on a water-bath in the partial vacuum produced by a good water-pump until formic acid ceases to distil over. Four or five hours is generally sufficient, although the heating may with advantage be prolonged for several additional hours. No frothing takes place, and the process requires little attention. When once begun, the heating should not be interrupted, as on cooling the mass becomes much more viscid, and being saturated with carbon dioxide frothing generally occurs on resuming the heating. This, however, is not serious, and by disconnecting the pump from time to time the liquid can be prevented from passing over into the receiver.

When nothing further distils over in the partial vacuum at 100°, the mixture is heated very slowly under the ordinary pressure over a wire gauze with a thermometer immersed in the liquid until the temperature reaches 240°. If the preliminary heating has been continued sufficiently long, only 5—6 c.c. should distil over before a temperature of 210° is reached; whatever passes over, however, may be rejected, as it is mainly water and formic acid.

When the temperature of the liquid reaches 220—225° rapid disengagement of carbon dioxide occurs, and allyl alcohol and allyl formate distil over in approximately equal amounts. The bulk of the decomposition occurs in the neighbourhood of 223°, and when 230° is reached it is practically complete. The reaction is at an end when liquid ceases to distil over, but the temperature should never be allowed to rise above 240°. The residue in the flask can then be made up to 500 grams by the addition of more glycerol, a further 500 grams of anhydrous oxalic acid can be added, and the process repeated. When this has been done four or five times it is best not to use the residue further, as it shows a tendency to froth during the preliminary heating.

If the final heating is carefully conducted and the temperature not allowed to rise above 235—240°, practically no acrolein is

produced, and the residue, consisting mainly of glycerol, is only slightly discoloured.

Owing to the extremely acrid nature of the volatile allyl formate, some of the vapour of which is carried through the condenser by the escaping carbon dioxide, it is best to pass the issuing gas through a small flask filled with lumps of ice, and then conduct it into a draught chamber or into the outer air. A small loss of allyl formate, which is condensed by the ice, is also thus prevented.

It is advisable when heating under the ordinary pressure to fit the flask with a short fractionating column, as otherwise some 30—40 grams of glycerol distil over and are lost. The exact amount thus distilling over depends on the rate at which the decomposition is effected. By using a column most of this glycerol, which would otherwise be wasted, is condensed, and returned to the distilling flask. A Young column with four pear-shaped bulbs is a suitable one to use.

In order to obtain allyl alcohol there is added to the liquid which distils over while the temperature rises from 210° to 235° a solution of 50 grams of sodium hydroxide in a litre of water, and the mixture is kept at the ordinary temperature for twelve hours or thereabouts in order to hydrolyse the allyl formate. The liquid is then distilled, and the first 300 c.c. passing over, which contain the whole of the allyl alcohol, are collected. By fractionating this distillate, the allyl alcohol can easily be obtained as a constant boiling mixture with water. This boils at 87 — 88° under the ordinary pressure, contains from 27 to 28 per cent. of water, and can be used for most purposes for which allyl alcohol is required. In this separation a fractionating column is necessary. A Young column with twelve pear-shaped bulbs answers the purpose well.

If such a column is not available a similar mixture of water and allyl alcohol can be separated from the 300 c.c. of distillate, as a lighter layer which floats on the surface, by adding 50 grams of anhydrous potassium carbonate.

If the allyl alcohol is required free from water the constant boiling mixture can be further dehydrated by adding from time to time small quantities of anhydrous potassium carbonate—about 10 grams is a convenient quantity to use—and discarding the heavy aqueous layer as long as one separates. When this no longer happens and the potassium carbonate remains solid after some hours, the allyl alcohol is filtered off and distilled, all that passes over below 96° being collected apart and re-dehydrated by potassium carbonate.

The remaining portion—generally more than half of the whole—

distils between 96° and 97° , and is practically pure allyl alcohol.

If the isolation of the allyl formate, present to the extent, roughly, of 50 per cent. in the original product of heating, be desired, it is best to distil this directly, using the twelve-bulb fractionating column, collecting apart all passing over below 87° . This, when washed a few times with a very little water to remove allyl alcohol, and dried over fused calcium chloride, gives on distillation pure allyl formate boiling at $82-83^{\circ}$ under the ordinary pressure.

It is generally possible, using 500 grams of glycerol and 500 grams of anhydrous oxalic acid, to obtain in one operation about 200 to 210 grams of the constant boiling mixture of allyl alcohol and water, or about 150 grams of pure allyl alcohol.

If the crude distillate from similar quantities is fractionated to obtain the allyl formate about 90 grams of the pure ester can generally be obtained.

The weight of the residue left after the decomposition of the dioxalin is usually somewhat less than half that of the glycerol used.

The yield of allyl alcohol in a carefully conducted experiment in which all the residues are worked up is practically theoretical, calculated on the amount of glycerol actually used up.

The distillate passing over during the preliminary heating on the water-bath in a vacuum contains a considerable quantity of formic acid, and can be used for the preparation of the salts of this acid.

The addition of a small quantity of ammonium chloride recommended by Tollens has not been found to be of any advantage; the yield of allyl alcohol, when the ordinary glycerol and oxalic acid of commerce are employed, is not thereby increased, whilst the glycerol left after the heating is considerably discoloured and rendered less suitable for repeated use.

UNIVERSITY CHEMICAL LABORATORY,
OXFORD.

[Received Feb. 18th, 1915].