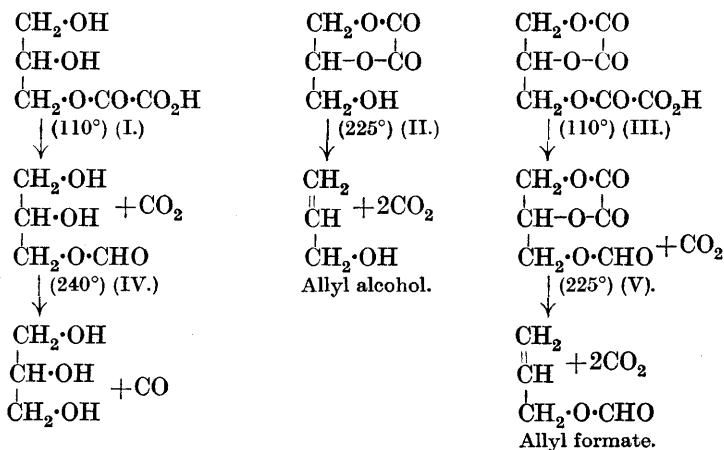


### CXLVIII.—*The Preparation of some Allyl Compounds.*

By SAMUEL COFFEY and CHARLES FREDERICK WARD.

FOR certain researches which are in progress in this laboratory the authors required considerable quantities of allyl chloride, and the present communication is the outcome of a study of the methods of preparing this compound.

The well-known process of Tollens for the production of allyl alcohol (*Annalen*, 1870, **156**, 129) is open to very serious objections and is probably based on a false conception of the reaction. A very large excess of glycerol is used and the amount of oxalic acid lost as carbon monoxide is also very large, consequently the yield is very poor. Chattaway (T., 1914, **105**, 151; 1915, **107**, 407) demonstrated that it was essentially by the decomposition of a dioxalin that allyl alcohol was produced and that the reactions between glycerol and oxalic acid appeared to be represented by the following scheme :



The oxalins I, II, and III are initially formed in varying proportions according to the conditions of the experiment. At higher temperatures (110°) the hydrogen oxalins give carbon dioxide and formins (IV and V). Dioxalin (II) and monoformin dioxalin (V), at higher temperatures still (220—225°), decompose into carbon dioxide and allyl alcohol and allyl formate respectively, whilst at still higher temperatures (240°) monoformin (IV) gives glycerol

and carbon monoxide. Formic acid is produced by the action of an excess of oxalic acid on the formins and distils during the second stage of the reaction. From this it is apparent that a relatively large amount of oxalic acid must be used in the preparation of allyl alcohol.

Chattaway (*loc. cit.*) drew these conclusions partly from a study of the action of ammonia and aniline on the products of the reaction and partly from the properties of the ethyl oxalates; the results of comparative experiments given below completely confirm the above scheme in every detail.

The experiments also clearly demonstrated the four consecutive reactions, and it was possible to convert nearly the whole of the glycerol in one operation into allyl alcohol and to account for more than 90 per cent. of the oxalic acid as free and combined formic acid, carbon dioxide, and water. The net loss, therefore, is negligible.

From the point of view of the student the usual methods of preparing formic acid and allyl alcohol are very uninteresting and unsatisfactory with regard to yield, time, and manipulation. Also the simple equation given in the text-books gives no clue as to where the loss occurs.

The method given below would seem to be far superior to the old method as a laboratory experiment. In the course of one day the student could, in one operation, obtain about 40 grams of formic acid as an approximately 50 per cent. solution, and 100 grams of pure allyl alcohol and at the same time follow the whole reaction and account for all his materials.

Allyl chloride is by far the cheapest allyl haloid, but the methods of preparing it leave much to be desired. Eltekow's method (*J. Russ. Phys. Chem. Soc.*, 1882, **14**, 394) is long and gives only a 50 per cent. yield, whilst the action of phosphorus trichloride on the alcohol gives mainly phosphorous esters and only 10—20 per cent. of allyl chloride. More recently, Bruylant (*Rec. trav. chim.*, 1909, **28**, 247) has improved the preparation by heating allyl alcohol and hydrogen chloride under pressure, but he gives no details of yield. Aschan (*Finska. Chem. Med.*, 1918, 3 pp.) finds that allyl chloride is obtained in good yield from allyl formate and hydrogen chloride in the presence of anhydrous zinc chloride. The authors' experiments show that, in the presence of condensing agents, the time of interaction of hydrogen chloride and allyl alcohol may be considerably shortened, but as a rule the yield of allyl chloride is very little better than that given by the older methods. The only condensing agent which is of any practical use is zinc chloride.

## EXPERIMENTAL.

*Preparation of Allyl Alcohol, Allyl Formate, and Formic Acid.*

Pure, hydrated, finely divided oxalic acid (500 grams) and anhydrous glycerol (250 grams) are mixed in a litre flask which is connected with a condenser and receiver. The latter is connected with a water-pump and exhausted to about 120—100 mm. The flask is then gently warmed. At about 60° (thermometer in the liquid) the mixture boils vigorously, becomes homogeneous, and water (more than 100 grams) distils. This is the first stage of the reaction, the formation of the oxalins I, II, and III, and usually takes one hour. The pressure then rapidly rises to 480 mm. and the thermometer remains stationary at 105—110° for some time. The vigorous ebullition ceases, a rapid effervescence of carbon dioxide sets in, and formic acid distils over with more water. There is no frothing if pure materials are used and the pressure is maintained below 500 mm. After one to one and a half hours, the pressure in the apparatus slowly falls to about 120 mm.; this indicates the end of the second stage, namely, the production of formins IV and V from the oxalins by loss of carbon dioxide and their subsequent decomposition into oxalins and formic acid by excess of oxalic acid. The temperature also rises to 190°, when distillation and evolution of gas almost cease. Quite suddenly, at 195—200°, the pressure increases rapidly. The receiver is then changed and the distillation carried on at the ordinary pressure. Carbon dioxide is again rapidly evolved, contaminated with some carbon monoxide and a negligible quantity of allyl formate. Allyl alcohol and allyl formate distil over together and the temperature remains stationary at 225° until distillation ceases, showing the end of the third stage of the reaction. The temperature then rises to 240°, when there is a rapid evolution of almost pure carbon monoxide. The last reaction ceases abruptly after about five minutes, and the colourless residue (80 grams) consists of glycerol. During the last two stages of the reaction the apparatus should be connected with a wash-bottle containing water, and the gases led into an efficient draught-chamber. If the rate of decomposition is allowed to become too rapid, a large amount of glycerol is liable to distil over. It will be seen from the above description that the changes on the manometer and the thermometer are accurate criteria of the transitions between the various stages of the reaction.

To obtain pure allyl alcohol, the crude allyl alcohol-formate mixture (150 grams) is boiled under reflux with 750 c.c. of 10 per

cent. sodium hydroxide solution for one hour and fractionated through a long column. All the allyl alcohol passes over below  $98^{\circ}$  and the distillate is dried with small quantities of anhydrous potassium carbonate. It is then distilled and should give 100 grams of pure allyl alcohol, b. p.  $95-97^{\circ}$ .

To obtain allyl formate, the crude allyl alcohol-formate mixture is washed several times with small quantities (20 c.c.) of water to remove allyl alcohol, and the insoluble ester dried over anhydrous calcium chloride. This on distillation gives a yield of pure ester, b. p.  $82-83^{\circ}$ , corresponding with 70 per cent. of the crude alcohol-formate mixture. The washings may be worked up for allyl alcohol in the usual manner.

Allyl formate may also be obtained by fractionating the crude product several times, but in this case only a 50 per cent. yield can be obtained. The formic acid in the first aqueous distillate (stages I and II) may be recovered either as a formate or as formic acid in the usual manner.

Thus, in one operation, 40 grams of formic acid and 100 grams of pure allyl formate, or about 100 grams of allyl alcohol, can be obtained from 250 grams of glycerol and 500 grams of hydrated oxalic acid.\* The residue of glycerol (80 grams) is quite suitable for further use.

The following table gives the results of comparative experiments performed exactly as described with different initial concentrations of glycerol and oxalic acid. It will be seen that these results are in complete accord with those required by the above reaction scheme, and may be summarised as follows.

1. The yield of allyl alcohol calculated on the glycerol actually used is always nearly theoretical.

2. As the amount of oxalic acid increases, the yield of allyl formate in comparison with allyl alcohol also increases. This is to be expected, because the larger amounts of oxalic acid are favourable to the production of dioxalin hydrogen oxalate (III), as is readily shown by a comparison of the amount of the alcohol-formate mixture with the yield of allyl formate. This was actually proved by isolating the allyl formate.

3. With increase of oxalic acid, the amount of free formic acid increases.

4. With increase of oxalic acid, the amount lost as carbon monoxide is diminished. This passes through a minimum in experi-

\* There is no necessity to use anhydrous oxalic acid in the above preparation (see Chattaway, *loc. cit.*), as all the water of crystallisation distils over during stages I and II. This effects a saving of several hours in the duration of the experiment.

ment 4, as in experiment 5 the loss increases again. In this experiment the amount of oxalic acid is relatively very large, and no doubt di- and tri-hydrogen oxalins would be produced in appreciable quantities, giving the corresponding formins and ultimately glycerol and carbon monoxide.

*Results of Comparative Experiments.*

	1.	2.	3.	4.	5.
	Grams.	Grams.	Grams.	Grams.	Grams.
Glycerol taken .....	400	350	350	250	200
Oxalic acid taken ...	275	350	500	500	500
Alcohol-formate mixture .....	40	88	110	150	110
Allyl alcohol .....	32	65	85	95	80
Free formic acid .....	7	13	25	36	42
Glycerol recovered ...	215	230	210	80	60
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Percentage of oxalic acid lost after calculating for free and combined formic acid, CO <sub>2</sub> and H <sub>2</sub> O	50	30	28	10	20
Percentage of formate in alcohol-formate mixture	35	40	60	70	75

The amount of carbon monoxide was relatively much larger with smaller amounts of oxalic acid. The quantitative results are not given, but it may be stated that in experiment 3 the ratio CO : CO<sub>2</sub> rapidly exceeded unity, whilst in experiment 4 this ratio was not reached until all the allyl alcohol had distilled. In experiment 5 the amount of carbon monoxide was larger for the reason already given.

*Preparation of Allyl Chloride.*

The best results were obtained as follows :

Allyl alcohol (46 grams) and anhydrous zinc chloride (20 grams) were mixed in a distillation flask immersed in a water-bath at 75—82°, and hydrogen chloride was passed into the mixture. The gas was rapidly absorbed and a liquid distilled. The end of the reaction was indicated by hydrogen chloride issuing from the end of the condenser. The crude distillate gave on fractionation : allyl chloride (35 grams) corresponding with a 60 per cent. yield, and 10 grams of diallyl ether, b. p. 90—95°. The experiment required only half an hour.

With aluminium chloride (anhydrous) alone, allyl alcohol reacts very vigorously, giving very little allyl chloride and a large tar-like residue.

When calcium chloride and allyl alcohol are mixed, an additive compound is obtained, which, when heated at 80—90° in a stream of hydrogen chloride, gives a product boiling at 90—92°. This is probably diallyl ether, and contains only a trace of chloride.

Aschan's method (*loc. cit.*) for the formation of allyl chloride was tried, but although the yield on the ester actually used is 80 per cent., the reaction is extremely slow, and it is advantageous to prepare the alcohol and then use the method given first in this paper. An experiment was made by saturating allyl alcohol in the cold with hydrogen chloride in the presence of zinc chloride. The yield was not improved, however, and the reaction required a long period for completion.

One of us (C. F. W.) wishes to express his indebtedness to the Department of Scientific and Industrial Research for a grant which is enabling him to carry out these investigations.

One of us (S. C.) makes acknowledgment to the Royal Commissioners for the 1851 Exhibition for the grant of a research scholarship.

CHEMICAL DEPARTMENT,  
UNIVERSITY COLLEGE, NOTTINGHAM. [Received, June 23rd, 1921.]

---