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PREPARATION OF ALLYL ALCOHOL AND ITS HOMOLOGUES

Franz Köhler, Darmstadt, Germany, assignor to Rohm & Haas Company, Philadelphia, Pa.

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4 Claims. (Cl. 260—640)

This invention relates to the preparation of allyl alcohol and its homologues.

It is known that allyl alcohol and its homologues can be made by saponification of allyl chloride and its homologues by means of alkaline saponifying agents. If, however, such a saponification is carried out in the usual manner, the yields obtained vary from about 30 to about 60% of the theory depending upon the choice of the alkaline medium such as caustic alkalies or alkali carbonates, if desired with a small addition of bicarbonate. In view of these poor yields it has already been suggested that the process might be improved by working at high temperatures under pressure. The technical application of this method, however, is subject to the usual disadvantages of processes carried out under pressure.

It has now been found that practically complete saponification can be obtained without the use of pressure or high temperatures by carrying out the saponification with alkaline media in the presence of metals which form complex compounds or in the presence of these complex compounds themselves. These materials catalyze the saponification reaction and apparently prevent the development of disturbing side reactions. Any of the usual alkaline media may be used; the preferred compounds, however, are alkaline reacting salts, particularly the alkali carbonates.

The metals which form complexes and which are operable in the present invention are, for example, cobalt, zinc, and copper, copper being particularly suitable. The metals must be used in finely divided form and during the course of the reaction go into solution, at least in part, in the form of complex compounds. The same effect is also obtained in the absence of metals if the corresponding complex compounds are employed. Complex compounds which are soluble in alkaline media are preferred. The process is particularly suitable for allyl alcohols substituted in the 2 position, such as 2-methyl allyl alcohol (methallyl alcohol) which may be used as a plasticizer for acrolein resins or for the preparation of methacrolein.

The invention may be illustrated by the following examples but it is not limited to the exact materials, times, temperatures, etc. indicated as it may otherwise be practiced within the scope of the appended claims.

Example 1

3.5 g. of copper powder and 50 g. of allyl chloride are added to a solution of 117 g. of potassium carbonate in 500 g. of water. The entire mixture is heated under a reflux condenser, while being stirred, to 80–85° C. On distilling this mixture 1.5 g. of low-boiling material is obtained and 34 g. of allyl alcohol corresponding to 90% of the theory.

If potassium hydroxide is used in place of potassium carbonate, somewhat lower yields (about 80%) are obtained, whereas without the addition of the copper powder yields of 33 and 46% respectively are obtained. It is to be noted that in the absence of copper powder the yields obtained with potassium hydroxide are greater than those with potassium carbonate.

Example 2

25 cc. of Ost's solution (containing 0.15 g. of copper) and 50 g. of methallyl chloride are added to a solution of 115 g. of potassium carbonate in 500 g. of water and the mixture heated under a reflux condenser, while being stirred, to 120–130° C. for two hours. On distillation 1.5 g. of low-boiling material and 37 g. of methallyl alcohol was obtained, corresponding to 93% of the theory. Without the addition of Ost's solution a yield of only 36% was obtained. Furthermore, if potassium hydroxide were used in place of potassium carbonate, a yield of only 29% of the theory was obtained. By using 3.5 g. of pulverized electrolytic copper in place of Ost's solution a yield of 96% was obtained.

For the following experiments a crude methallyl chloride was used which is obtained by the chlorination of technical isobutylene. It contained 57% of pure methallyl chloride, the remainder being high-boiling chlorides.

Example 3

10 g. of zinc filings activated with copper sulfate and 50 g. of crude methallyl chloride were added to a solution of 100 g. of crystallized sodium carbonate in 500 g. of water and the entire mixture stirred and heated two and one-half hours under a reflux condenser at 120–130° C. On distillation there was obtained 4 g. of low-boiling materials and 20 g. of methallyl alcohol corresponding to 88% of the theory.

Example 4

3.5 g. of pulverized electrolytic copper and 50 g. of crude methallyl chloride were added to a solution of 115 g. of potassium carbonate and 500 g. of water and the mixture stirred one hour under a reflux condenser at 110–120° C. On dis-

tillation 22.5 g. of methallyl alcohol was obtained corresponding to 100% of the theory.

I claim:

1. The process of preparing allyl alcohol and its homologues from the corresponding chlorides which comprises saponifying said chlorides with an alkaline saponifying agent selected from the group consisting of alkali metal hydroxides and carbonates while in the presence of a complex compound formed from a metal from the group consisting of zinc, cobalt, and copper and said alkaline saponifying agent.

2. The process of preparing allyl alcohol and its homologues from the corresponding chlorides which comprises saponifying said chlorides with an alkaline saponifying agent selected from the group consisting of alkali metal hydroxides and carbonates while in the presence of a finely divided metal from the group consisting of zinc, cobalt, and copper, which metal forms in situ a complex compound.

3. The process of preparing allyl alcohol from allyl chloride which comprises saponifying allyl chloride with an alkaline saponifying agent selected from the group consisting of alkali metal hydroxides and carbonates in the presence of finely divided copper which forms in situ a complex copper compound.

4. The process of preparing methallyl alcohol from methallyl chloride which comprises saponifying methallyl chloride with an alkaline saponifying agent selected from the group consisting of alkali metal hydroxides and carbonates in the presence of finely divided copper which forms in situ a complex copper compound.

FRANZ KÖHLER.