

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE CONVERSION OF ALDEHYDES CONTAINING A VINYL GROUP INTO THE CORRESPONDING ALCOHOLS

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The present invention relates to improvements in the production of unsaturated alcohols from unsaturated aldehydes which contain a vinyl group in the end position.

It is an object of the present invention to provide a process for the reduction of unsaturated aldehydes of the type of acrolein containing a vinyl group in the end position to the corresponding unsaturated alcohols wherein the production of saturated alcohols is minimized.

The present process is especially advantageous in the production of allyl alcohol from acrolein or allyl alcohol homologues from homologues of acrolein, such as, for example, the production of alpha-methyl-allyl alcohol from alpha-methyl acrolein.

In accordance with the present invention, the unsaturated aldehydes are reduced with the aid of aluminates of secondary alcohols which contain at least four, and preferably five to eight, carbon atoms. The conversion is easily achieved merely by mixing the reaction components and slight heating of the mixture. In many instances the heat of reaction which is produced by the admixture of the reaction components renders it unnecessary to employ supplemental heating. The proportions of the reaction components may be varied, but it has been found preferable to employ molar proportions or to provide an excess of the aldehyde.

It has been found that good results may be obtained if the unsaturated aldehyde is employed in excesses of up to 50%.

In production of the aluminum alcoholates, it has been found advisable to employ an excess of alcohol. The resulting alcoholic aluminate solution has been found very suitable for the reduction. The reduction, furthermore, may be carried out in the presence of inert diluents, but this precaution is generally not necessary.

The ketone which is obtained from the aluminate during the reduction of the aldehyde may be reduced to the secondary alcohol by known hydrogenation processes. The losses in the alcohol are very small, and it may be re-used again in the form of its aluminate for the conversion of the aldehyde in accordance with the present invention.

The conversion in accordance with the present invention is rapid. The reaction mixture which is obtained essentially contains only the desired unsaturated alcohol and the ketone which is formed from the aluminate. The unsaturated alcohol and the ketone are easily separated, if

necessary, after acidification with sulfuric acid by simple fractionation.

In accordance with the present process, vinylated aldehydes, as, for example, butene-1-al-4, pentene-1-al-5, hexene-1-al-6, 3-methyl-pentene-1-al-5 and the like, may be converted into their corresponding unsaturated alcohols. The present process is especially applicable to the conversion of acrolein and its homologues, such as alpha-methyl acrolein or alpha-propyl acrolein. Examples of secondary alcohols, the aluminates of which may be employed as the reducing agent in accordance with the present invention, are as follows: Methyl-n-amyl carbinol, ethyl-n-propyl carbinol, methyl-isopropyl carbinol, ethyl-isopropyl carbinol and phenyl-n-ethyl carbinol.

Previous processes, when applied to the preparation of unsaturated alcohols from aldehydes containing a vinyl group, were not satisfactory in view of the fact that too strong a reduction is obtained whereby saturated alcohols are obtained in addition to the desired unsaturated alcohols. The production of these undesired saturated alcohols does not only lower the yield of the unsaturated alcohols, but also is very disturbing in that the saturated alcohols hinder the recovery of the unsaturated alcohols from the reaction mixture.

The process in accordance with the present invention suppresses undesired side reactions almost entirely, especially in the preparation of allyl alcohols from acrolein. This was not to be expected, especially in view of the fact that the starting materials in question are also easily converted into polymerization or condensation products. However, no polymerization or condensation of the starting materials can be ascertained in the process in accordance with the present invention.

For the success of the process in accordance with the present invention, it is necessary that the alcohol from which the aluminate is prepared is a secondary alcohol and contains at least four carbon atoms. For example, if acrolein is reduced with isopropyl aluminate, the strong reducing action obtained produces substantial quantities of the undesired n-propyl alcohol.

The following examples serve to illustrate the present invention:

Example I

During thirty minutes, 440 grams of 97% acrolein were allowed to run into the alcoholic aluminate solution obtained by dissolving 150 grams aluminum in 3000 grams methyl-n-amyl carbinol,

while stirring. The reaction is strongly exothermic in the beginning, and the reaction temperature was maintained between 65° C. to 75° C. by cooling. After the total quantity of acrolein was added to the aluminate solution, the reaction mixture was heated to 90° C. to complete the reduction. After cooling the resulting mixture to 40° C., the calculated quantity of aqueous sulfuric acid is added and the oily layer is decanted from the aqueous aluminum sulfate layer. The small quantities of the ketone and allyl alcohol contained in the aqueous layer were recovered by steam distillation and added to the decanted oily fraction. After drying, the oily fraction was subjected to fractional distillation. Substantially pure allyl alcohol was obtained having a boiling point 96° C. to 97° C. (K_p 760). The yield obtained was 366 grams from the 440 grams of 97% acrolein which were employed or, in other words, a yield of 82.8%. Even higher yields have been obtained when carefully controlled reaction conditions were employed.

Example II

While stirring and cooling, 46 grams of alpha-methyl acrolein were run into an alcoholic aluminate solution prepared from 18 grams aluminum and 219 grams methyl-n-butyl carbinol. After the end of the reaction, the reaction mixture was heated to 95° C. for a short period of time. After cooling the resulting reaction mixture, it was treated with an amount of aqueous sulfuric acid necessary for the decomposition of the aluminate. The oily layer was then separated from the aqueous aluminum sulfate solution. The oils obtained, including the portion recovered from the aqueous layer by steam distillation, were then dried with potassium carbonate and rectified. Substantially pure alpha-methyl-allyl alcohol having a boiling point 113° C. to 114° C. (K_p 760) was obtained. The yield amount to 37 grams or 81.5% of the theoretical.

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