

# ALIEN PROPERTY CUSTODIAN

## PROCESS FOR THE PRODUCTION OF HIGHER MOLECULAR ALDEHYDES AND ALCOHOLS

Rudolf Kern, Ludwigshafen-on-Rhine, Germany;  
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The present invention relates to a process for the production of higher molecular aldehydes and alcohols.

It is already known that crotonaldehyde may be condensed to higher molecular unsaturated aldehydes by means of condensing agents such as amines and salts of amines, preferably in the presence of an excess of a weak acid. This condensation, however, generally delivers but an insufficient yield of higher molecular aldehydes because crotonaldehyde or the resulting polyenealdehydes tend to form undesirable cyclic substances or resins. The higher molecular alcohols, prepared from the condensation products in known manner by catalytic hydrogenation, thus leave a considerable residue of resinous substances when distilling.

I have now found that the said disadvantages may be overcome and higher molecular aliphatic aldehydes and alcohols may be obtained in a very good yield by carrying out the first step of the reaction, i. e. the condensation of the crotonaldehyde to higher molecular aldehydes, wholly or in part in the presence of active hydrogen under so mild conditions that no substantial hydrogenation of the aldehyde group occurs. The term "active hydrogen" is intended to comprise hydrogen in statu nascendi or hydrogen made active by the presence of catalysts. The aldehydes thus prepared may be reduced by subsequent treatment with hydrogen under energetic conditions. The formation of undesirable by-products, especially resins, is practically completely avoided by this method of working. There are mainly obtained straight-chained saturated or only partly unsaturated aliphatic aldehydes or alcohols, respectively.

As condensing agents suitable for the purposes of the present invention there may be mentioned for example salts of amines, especially of secondary amines, preferably in the presence of an excess of a weak acid, or acid salts from polycarboxylic acids and secondary amines. Suitable salts of the said kind, for example, are those of diethylamine, methylethylamine, dibutylamine, methylcyclohexylamine, dicyclohexylamine, diethanolamine, dimethylethylenediamine, dihydroxyethylhexamethylenediamine, heterocyclic bases, such as piperidine, morpholine and pyrrolidine. Primary amines are also suitable as condensing agents, but have a tendency to cause the formation of nitrogen-containing condensation products. The salts of the amines may contain as the acid component, for example, formic acid, acetic acid, crotonic acid, succinic acid or adipic acid; mixtures of salts of the said kind may also be used as condensing agents.

The condensation may be carried out in the presence or absence of solvents or diluents, as for example methanol, ethanol, butanol, dioxane

or other ethers and alcohols. Since heat is evolved during the reaction, care should be taken to regulate it by cooling and stirring. The temperature during the condensation should be kept below 80° C, advantageously between 20 and 70° C. It is often advisable to remove the water resulting in the condensation, e. g. by the addition of agents capable of binding water or by azeotropic distillation.

The condensation may be carried out under normal conditions or under superatmospheric pressure. It may be carried out in the presence of hydrogenation catalysts, for example chromium-activated nickel catalysts or by using hydrogen in statu nascendi, for example hydrogen obtained from the reaction between zinc and acids, in particular acetic acid, or by the addition of aluminum, activated by means of mercury, which combines with the water formed in the condensation, thus liberating hydrogen which in turn is saturating part of the double linkages of the polyenealdehydes.

One method of carrying out my invention consists in that the crotonaldehyde is condensed by allowing a secondary amine, as for example piperidine or morpholine, to run slowly into a mixture of crotonaldehyde and an acid, for example acetic acid. Another method consists in that the crotonaldehyde is allowed to run into a solution of a secondary amine in an excess of acid in small portions, while suspending the addition of further amounts of crotonaldehyde, until the red-colored polyenealdehydes first formed have been hydrogenated into colorless products. Finally crotonaldehyde may also be added continuously at such a speed that no red color caused by polyenealdehydes is observed. When employing other condensing agents, the mode of operation may be modified in a suitable way. It is understood that, regardless of the method of bringing together the reactants, the condensation is carried out at least partly in the presence of active hydrogen.

The aldehydes obtained in the first step of this invention may be directly hydrogenated to alcohols, if desired after previously separating the condensing agents. This second step is carried out under so energetic conditions that the



group of the aldehydes is converted into the  $-\text{CH}_2\text{OH}-$  group, by using ordinary or increased pressure and working, for example, at a temperature above 80° C, preferably between 120° and 200° C, in the presence of the usual hydrogenation catalysts. When employing pressures of between 50 and 250 atmospheres, the hydrogenation

of the aldehyde mixture to alcohols proceeds very smoothly.

The following examples serve to illustrate how the present invention may be carried out in practice, but the invention is not restricted to these examples. The parts are by weight.

*Example 1*

350 parts of crotonaldehyde are dissolved in 900 parts of methanol and 60 parts of glacial acetic acid and 50 parts of a Raney-nickel catalyst are added to the solution. Then 25 parts of piperidine are allowed to run into the solution in portions and, as soon as the temperature rises, hydrogen is introduced through a sieve plate while stirring. The temperature slowly rises to from 50° to 55° C; if the temperature should rise too rapidly, there is slightly cooled. Stirring is then continued for another 12 hours while introducing hydrogen. In order to gain the resulting hydrogenated aldehydes, the reaction mixture is filtered; after evaporating the solvents the residue is distilled under reduced pressure. In order to gain alcohols in the second step of the reaction the distilled aldehyde mixture may be reduced, if desired in the presence of a solvent, like methanol, by means of hydrogen and a hydrogenation catalyst at a temperature between 130° C and 190° C and a pressure of 50 to 100 atmospheres. The aldehyde mixture may also be reduced with hydrogen by means of a hydrogenation catalyst without distillation after removing the hydrogenation catalyst used during the condensation and the nitrogen-containing substances.

The alcohol mixture obtained by the second step of the reaction may be distilled under reduced pressure. The main fraction distills between 90° and 290° C under a pressure of 2 milli-

5 meters. These alcohols obtained in a good yield crystallize in part. Upon sulphonation or oxethylation they yield highly capillary-active products, the properties of which are analogous to those of the sulphonates or oxethylation-products respectively of fatty alcohols.

*Example 2*

875 parts of crotonaldehyde, 150 parts of glacial acetic acid and 125 parts of a chromium-activated nickel catalyst are charged in a stirring autoclave. After deaerating three times by means of nitrogen, 50 atmospheres of hydrogen are pressed in at a temperature of 20° C. From a pressure-vessel communicating with the autoclave 60 parts of piperidine are pressed into the reaction mixture in the course of some hours. At the outset of the condensation the pressure begins to drop, whereas the temperature rises. It is kept at between 35° and 40° C by cooling. After 2 hours the hydrogen pressure is increased to 115 atmospheres, whereupon the temperature is allowed to drop to a slight extent, until the absorption of hydrogen per hour has fallen to one third of the quantity hourly absorbed at the outset of the reaction. The reaction mixture is then slowly heated to 35° to 40° C, whereupon the absorption of hydrogen intensifies. After about 25 hours the condensation is practically finished.

30 The reaction mixture containing mainly saturated higher molecular aldehydes may be converted into higher molecular alcohols without separating the aldehydes. For this purpose the autoclave is slowly heated to 180° C until no more hydrogen is consumed. The yield of alcohols boiling above 160° C amounts to about 70 per cent of the theory.

RUDOLF KERN