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PROCESS FOR THE PREPARATION OF SIX MEMBERED N-HETEROCYCLIC COMPOUNDS FROM ACROLEIN OR ITS HOMOLOGUES AND AMMONIA

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The present invention relates to an improved process for the production of six membered N-heterocyclic compounds from acrolein or its homologues and ammonia.

The object of the present invention is to provide an economical and efficient process for the production of six membered heterocyclic compounds from acrolein or its homologues and ammonia.

Several syntheses for the production of six membered heterocyclic compounds from acrolein and ammonia, which, for the greater part, are carried out in the liquid phase, are known. However, all of these syntheses have led only to the most complex mixture of a great variety of substances, and six membered heterocyclic compounds were obtained in such minute quantities in these mixtures that the use of these processes upon a commercial scale for the production of these heterocyclic compounds was not feasible.

It has now been discovered that the valuable six membered heterocyclic compounds could be obtained in good yields by passing acrolein and ammonia in the vapor phase in admixture with an inert diluent over dehydration catalysts. The diluents which may be employed are, for example, hydrocarbons or their derivatives, such as benzene, homologues, gasolene, methanol, and steam. Steam has been found to give especially good results as it tends to activate the catalyst and to speed the reaction.

Besides acrolein, such acrolein derivatives as alpha-methyl acrolein, alpha-ethyl acrolein, phenyl acrolein and cinnamic aldehyde and the like may be employed.

The proportions of acrolein and ammonia employed may be varied within wide ranges. It is advisable, however, to employ an excess, preferably a large excess, of ammonia.

The proportion of diluent with respect to both other reaction components may also be varied within wide limits. However, as the addition of the inert diluent in accordance with the present invention produces a substantial increase in the yield of the heterocyclic bases and, at the same time, reduces resin formation and increases the lift of the catalyst, it is advisable not to have the proportion of the inert diluent too small. Good effects are, for example, obtained when employing a quantity of steam which is about one-half the weight of the other components of the reaction mixture. However, good results are also obtained when employing smaller quantities and substantially greater amounts of steam. The preferable proportions are between 2–20 times of diluent with respect to the acrolein.

If no diluents are employed, such as, for example, when leading a mixture of only acrolein and ammonia over aluminum oxide, large quantities of resin are obtained which causes the reaction to cease in a very short time.

The dehydration catalyst employed in accordance with the present invention may, for example, be aluminum oxide, active silica, aluminum phosphate, zinc phosphate, and the like. The dehydration catalysts may be employed in any desired combination with each other and may also be placed on carriers such as asbestos, active charcoal, and the like.

The reaction temperatures employed in accordance with the present invention generally lie between 200° C. and 600° C. Preferably temperatures between about 250° C. and 400° C. are employed.

In some cases it is advantageous to pass the substances over the catalyst with not too long a period of contact with the catalyst. For example, good results are obtained when ½ mol of the substrate and more, preferably 1 mol, is passed over per liter of contact mass per hour. Such liter of contact mass is measured as the amount of contact mass which will be required to fill a liter container when poured in and not compacted. The period of contact of the reaction components with the catalyst during their passage through the catalyst mass preferably is between 1 and 10 seconds.

A modification of the invention resides in adding saturated aldehydes, such as formaldehyde and acetaldehyde, to the reaction mixture. In this manner it is possible to influence the type of product obtained. For example, in accordance with the invention a mixture of acrolein, ammonia and steam will produce picoline, whereas if acetaldehyde is added to this reaction mixture increased quantities of pyridine are obtained.

The following examples serve to illustrate the present invention, but it is in no way limited thereto:

Example 1

A mixture of 200 cubic centimeters of 93% acrolein were passed, together with an excess of ammonia, through a V2A contact tube filled with 800 cubic centimeters of aluminum phosphate at a temperature of 300° C. for seven hours. During this experiment 200 grams of steam were introduced into the reaction mixture. The quantity of ammonia consumed was 280 grams. The condensate was salted out with sodium hydroxide

and the oil which separated was dried over barium oxide. The yield was 89.8 grams of picoline having a boiling point of 130° C. to 145° C. or 69% of the theoretical.

Example 2

A mixture of 18% aqueous acrolein and 280 grams ammonia was passed over aluminum oxide in a contact tube. The temperature employed was 375° C. The yield was 73.5 grams of picoline having a boiling point of 130° C. to 145° C. or 74% of the theoretical.

Example 3

A mixture of 112 grams of acrolein (95%), 88 grams of acetaldehyde, 250 grams ammonia and 200 grams of steam was passed over aluminum oxide in a V2A contact tube for six hours at a temperature of 380° C. A yield of 38.5 grams of pyridine having a boiling point of 100° C. to 125° C. was obtained.

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