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PROCESS FOR THE PRODUCTION OF CARBOXYLIC ACIDS OF THE PYRIDINE SERIES

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The present invention relates to a new process for the production of carboxylic acids of the pyridine series.

Carboxylic acid esters of the pyridine series, such as collidine dicarboxylic acid esters, are known to be difficultly attacked by aqueous solutions of alkali metal hydroxides, even if kept boiling for some time. Their saponification with alcoholic caustic alkali solutions proceeds smoothly but in this case the drawback exists that the alkali metal salts, in order to recover the free acids, must be converted into the lead or silver salts from which the acids are liberated by means of hydrogen sulphide. Such a multistage process, however, is uneconomic and, moreover, does not give satisfactory yields.

We have now found that carboxylic acid esters of the pyridine series can be converted into the free carboxylic acids in a simple manner and with good yields by heating the esters in the presence of water under pressure at a temperature of at least about 150° C. This course of the reaction is surprising since the esters are difficultly attacked even by aqueous solutions of alkali hydroxides, as stated above.

According to the present invention it is possible to obtain pyridine mono-, -di- and -polycarboxylic acids or their homologues, as for example lutidine-mono- or -dicarboxylic acid or collidine-mono- or -dicarboxylic acid, from their esters. Since in the synthesis of compounds of the pyridine series such esters are directly obtained (for example collidine dicarboxylic acid esters by condensing aldehyde-ammonia with acetic acid ester and oxidizing the dihydrocollidine dicarboxylic acid ester first obtained) the process according to the present invention provides a simple way for preparing the free carboxylic acids of the pyridine series.

The saponification is carried out, for example, at a temperature of between 150 and 200° C. The amount of water employed is advantageously from 4 to 6 times that of the ester. Usually the reaction mixture is simply heated in a closed vessel. The pressure may, however, be increased by pressing inert gases into the reaction space. After cooling, the greater part of the acids formed frequently crystallizes out and may be obtained by filtration, by centrifuging etc. An additional amount of carboxylic acid can be obtained by concentrating the mother liquor, if desired in vacuo.

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

Example 1

400 parts of collidine dicarboxylic acid diethyl ester and 2500 parts of water are heated in an iron pressure vessel for 24 hours at from 160° to 180° C. After cooling, the main part of the collidine dicarboxylic acid formed has crystallized out and is filtered off. By evaporating the mother liquor down to half its volume further acid is obtained. By recrystallizing the crude product from a little water while adding animal charcoal, 120 to 140 parts of pure collidine dicarboxylic acid are obtained crystallizing in the form of fine felted needles. As bye-products collidine monocarboxylic acid and collidine are recovered.

Example 2

30 parts of nicotinic acid ethyl ester and 180 parts of water are heated at a temperature of from 150° to 160° C for 20 hours. On cooling the reaction mixture, part of the nicotinic acid crystallizes out which is filtered off. A further amount of acid may be caused to crystallize by concentrating the mother liquor to half its volume. About 13 to 14 parts of nicotinic acid are obtained. By recrystallizing it from water it is obtained in a pure state.

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