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COMPLETE SPECIFICATION

Process for Producing Aldehydes

We, GUILIO NATTA and ENRICO BEATI, both of Italian Nationality, both of via Mario Pagano, 54, Milan, Italy, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statemen:—

This invention relates to syntheses in which a mixture of hydrogen and carbon monoxide reacts with compounds containing olefinic linkages to give products having one more carbon atom in the molecule than the original compounds.

It is known that hydrogen and carbon monoxide will react, in the presence of a catalyst, with compounds which contain an olefinic linkage such as the olefins themselves, or the unsaturated carboxylic acids, to produce saturated aldehydes in which the aldehyde group becomes attached to one of the carbon atoms of the olefinic linkage.

In the processes hitherto described, the synthesis progresses but slowly at a pressure as low as 20 atmospheres, and it has been customary to employ pressures in the neighbourhood of 200 atmospheres in order to obtain a satisfactory rate of reaction.

The rate at which the synthesis takes place is apparently determined by the rate of diffusion between the gaseous and liquid phases and the surface of the solid phase represented by the catalyst. This diffusion rate becomes higher with increase in pressure since at high pressure the rate of molecular bombardment is increased. It has now been found that the same effect may be achieved by subjecting the reaction mixture to vigorous agitation thereby making it possible to achieve a satisfactory rate of synthesis at pressures as low as 10 atmospheres.

The present invention provides a process for the production of an aliphatic or cycloaliphatic aldehyde which comprises reacting hydrogen, carbon monoxide and an olefin, a cycle-olefin, an olefinic carboxylic acid in which the olefinic linkage is not immediately adjacent to the carboxyl group, or an ester of such an acid at a temperature of at least 80° C. under a pressure of at least 10 atmospheres but below 50 atmospheres and with agitation in the presence of a cobalt-containing catalyst for the reaction, the olefin, cycloolefin, acid or ester having a saturation vapour pressure of not more than one atmosphere at the temperature of the reaction and having at least one hydrogen atom attached to each carbon atom of the olefinic linkage.

The required degree of agitation may be obtained either by fitting the reaction vessel with an internal stirring device of conventional design, or by confining the liquid components with the catalyst in suspension in a tall narrow tube, and forcing the mixture of gases upwardly therethrough.

The cobalt-containing catalysts used in the low pressure synthesis of the present invention are similar to those normally used in reactions of this type. It is preferred however to use partially reduced cobalt oxide, activated with small amounts (about 2%) of another metallic oxide or oxides which is less easily reducible than cobalt oxide. Ferric oxide is a preferred activator. The catalyst may for convenience be supported upon a finely divided inert material, for example a diatomaceous earth such as kieselguhr or a clay such as bentonite. Traces of nickel in the catalyst do not affect the synthesis but manganese oxide is definitely harmful. The cobalt and iron may be precipitated simultaneously upon the supporting material as their basic carbonates, which can then be decomposed thermally to form the oxides. This thermal decomposition may, if desired, be carried out in a stream of hydrogen at 350° C. so that the cobalt oxide is prepared and partially reduced in one operation.

[Price 2/-]

Normally gaseous and low boiling liquid olefins cannot be reacted in accordance with the present invention. To react, the olefin must have a saturation vapour pressure of not more than one atmosphere at the temperature of the reaction. As the temperature employed is preferably between 100° C. and 110° C. only those olefins which at atmospheric pressure boil at temperatures substantially within or above this range may be used. In general the molecular weight of most of the olefins which may be used is in excess of 100. The presence of substituents or additional multiple linkages in the molecule may have very deleterious results on the rate, or on the course, of the reaction. For instance, certain hydroaromatic compounds such as tetrahydronaphthalene, as well as styrene and stilbene show no reaction, while hydroaromatic compounds having a cyclo-olefinic nucleus such as dihydronaphthalene react readily. Compounds containing alcoholic or aldehydic groups either do not take part in the reaction, or are so susceptible to secondary reactions as to render the process inapplicable in practice. This is also true of compounds which have a carboxyl group immediately adjacent to the double bond. If however the ethylenic bond and a carboxyl group are widely separated in the molecule, the synthesis proceeds in the normal way, and at a rate which is satisfactory for practical purposes. This is especially true when the carboxyl group is esterified as in the methyl or glyceryl esters of oleic acid.

At temperatures between 80° C. and 110° C. the synthesis proceeds to the aldehyde stage with very little reduction of the aldehyde group to an alcoholic group. The preferred range of temperature is from 100° C. to 110° C., since below 100° C. the synthesis proceeds only slowly. When it is desired to convert the aldehyde group by reduction, to an alcoholic group, the aldehyde product need not be first purified. It is only necessary to increase the temperature in the reaction vessel to above 140° C. while continuing to maintain the gases at their pressure of from 10 to 20 atmospheres. Instead of continuing with the same gaseous mixture as was used in the aldehyde synthesis a mixture containing an increased proportion of hydrogen, or pure hydrogen itself may be substituted with advantage. It will be noted that no change in the composition of the catalyst has to be made when the temperature is changed to obtain reduction. Esters of hydroxy acids, from which the acids themselves may be liberated by saponification, may be obtained by this method.

The same catalyst, preferably reduced in amount, may also be used to oxidise the aldehyde when desired. In this case the aldehyde, mixed with solid catalyst, is taken, from the reaction vessel, and decanted from the bulk of the catalyst. Air or oxygen is then blown through the suspension in the aldehyde, of the remaining catalyst. This process is of particular value for the simple and economical production of half esters of dicarboxylic acids. These half esters may be saponified to form the free dicarboxylic acids which may be condensed with polyhydric alcohols to produce valuable synthetic resinous products.

The hydrogen and carbon monoxide used in the synthesis are best mixed in approximately equimolar proportions. They should be as free as possible from traces of oxygen which when present has a retarding effect on the process.

The following examples illustrate the manner in which the invention may be carried into effect:—

EXAMPLE I.

Into a tank having a capacity of about 3 litres, provided with a mechanical stirring device controlled from the outside and capable of withstanding a pressure of 20 atmospheres, there is introduced 1 kg. of 1-octadecene together with 100 gr. of catalyst. The catalyst is prepared by simultaneous thermal decomposition and partial reduction with hydrogen at 350° of a mixture of the basic carbonates of cobalt, (98%) and iron (2%). This mixture is obtained by simultaneous precipitation from an aqueous solution of the corresponding metallic nitrates with potassium carbonate on to a support of kieselguhr.

A mixture of carbon monoxide and hydrogen, at a pressure of 12 atmospheres, and free from traces of oxygen, is introduced into the tank. The mixture is heated to between 100° C. and 110° C. with the stirring device in operation and a further supply of the carbon monoxide and hydrogen mixture is added as the latter is absorbed by the reaction, so as to maintain the pressure between 15 and 20 atmospheres. The operation is continued until no more gas is absorbed.

The reaction product consists mainly of α-methyl-octadecyl- and nonadecyl-aldehydes, containing small quantities of the corresponding alcohols as impurities.

EXAMPLE II.

By employing the same conditions as in Example I, but using, instead of octadecene, hydroaromatic compounds having a cyclo-olefinic nucleus, such as pinene or dihydronaphthalene, hydroaromatic aldehydes are obtained, which

contain one more carbon atom than the hydrocarbons from which they are derived.

EXAMPLE III.

The catalyst used in this case is prepared by precipitation of a mixture of 98% basic cobalt carbonate and 2% basic iron carbonate on a support of from 3 to 4 parts by weight of bentonite. Before use the catalyst is dried and partially reduced with hydrogen at 350° C.

Two kg. of methyl oleate, containing in suspension 300 gr. of catalyst, are introduced into a chrome-steel tube 3 metres high having a bore of 40 mm. and capable of withstanding a pressure of at least 20 atmospheres. The tube is heated to between 100° and 110° C. by means of an outer steam jacket. A pre-heated gaseous mixture, consisting of one volume of carbon monoxide and one volume of hydrogen, at 18 atmospheres pressure is circulated at the rate of 200 litres per hour. The circulation is maintained until no further gas absorption is observed.

The reaction product is decanted and filtered in order to separate the catalyst. It consists mainly of a mixture of 9-aldehydo- and 10 aldehydo-methyl stearates. The reaction product, freed by decantation from a part of the catalyst (which can then be used for further operations), is oxidised with air which is forced to bubble under pressure through the liquid kept at a temperature of about 100° to 150°. A mixture of methyl half esters of diacids is formed without any interruption in the chain of the organic molecule. For this purpose it is not necessary to add a specific oxidation catalyst, since the catalyst used for the former operation acts also in this manner.

EXAMPLE IV.

Into a 5 litre copper-lined steel pressure tank, fitted with a stirring device, are introduced 2 kg. olive oil and 300 gr. of the same catalyst as in the preceding example.

A mixture of carbon monoxide and hydrogen is introduced at a pressure of 12 atmospheres and the whole is heated to 110° C., giving a pressure of from 15 to 20 atmospheres, with operation of the stirring device. As the reaction proceeds more carbon monoxide and hydrogen mixture is supplied in order to maintain the pressure in the reaction vessel. The operation is continued until no more gas is absorbed. The product obtained consists of glycerides of aldehydo-stearic acids. By increasing the temperature during or at the end of the operation up to 150°—160° C., methylolstearic acid glycerides are mostly obtained. Their production is facilitated by adding hydrogen to the carbon monoxide and hydrogen mixture used in the first reaction, when the latter is completed, and by raising the temperature.

EXAMPLE V.

Into a pressure tank, similar to the one used in the preceding example, are introduced 2 kg. of grape-stone oil and 300 gr. of catalyst prepared as in Example I. The carbon monoxide and hydrogen mixture is introduced as in Example II, heating however to a temperature of 150° C. When the absorption has nearly ceased, the carbon monoxide and hydrogen mixture is released and the vessel flushed with hydrogen. Hydrogen is forced in until a pressure of 18 to 20 atmospheres is reached. The temperature is maintained between 150° and 160° C. until no more hydrogen is absorbed. The reaction product consists of glycerides of hydroxy acids, which on saponification with soda and treatment with dilute sulphuric acid yield a mixture of free hydroxy acids containing at least 19 carbon atoms in the molecule.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of an aliphatic or cycloaliphatic aldehyde which comprises reacting hydrogen, carbon monoxide and an olefin, a cyclo-olefin, an olefinic carboxylic acid in which the olefinic linkage is not immediately adjacent to the carboxyl group, or an ester of such an acid at a temperatue of at least 80° C. under a pressure of at least 10 atmospheres but below 50 atmospheres and with agitation in the presence of a cobalt-containing catalyst for the reaction, the olefin, cyclo-olefin, acid or ester having a saturation vapour pressure of not more than one atmosphere at the temperature of the reaction and having at least one hydrogen atom attached to each carbon atom of the olefinic linkage.

2. A process according to claim 1 in which the reaction temperature is between 100° C. and 110° C.

3. A process according to either of claims 1 or 2 in which the pressure employed is between 10 and 20 atmospheres.

4. A process according to any one of claims 1 to 3 in which the catalyst is partly reduced cobalt oxide activated with another metallic oxide such as ferric oxide.

5. A process according to claim 4 in which the catalyst is supported upon finely divided inert material.

6. A process according to any one of the preceding claims in which the agita-

tion is effected by forcing a mixture of hydrogen and carbon monoxide through the liquid.

7. A process according to any one of the preceding claims in which the ester is a methyl or glyceride ester.

8. A process according to any one of the preceding claims in which an olefinic carboxylic acid or an ester thereof is employed and the resulting aldehyde is thereafter reduced with hydrogen in the presence of the same catalyst to the corresponding hydroxy acid or ester.

9. A process according to claim 8 in which the hydrogen used for reduction is mixed with carbon monoxide.

10. A process according to any one of claims 1 to 7 in which an olefinic carboxylic acid or ester thereof is employed and the resulting aldehyde is thereafter oxidised with oxygen in the presence of at least part of the same catalyst to produce the corresponding dicarboxylic acid or half ester thereof.

11. A process according to any one of the preceding claims in which the free aldehydo-, hydroxy-, or di- carboxylic acid is prepared by saponification of its ester.

12. The process as herein described with reference to any one of the Examples.

13. Aliphatic and cycloaliphatic aldehydes; hydroxy-, aldehydo-, and dicarboxylic acids and their esters; when prepared by the processes of the preceding claims.

Dated this 7th day of August, 1946.

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