United States Patent Office 3,108,142 Patented Oct. 22, 1963

3,108,142

CATALYTIC HYDROGENATION OF CARBOCYCLIC COMPOUNDS HAVING OLEFINIC DOUBLE LINKAGES

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No Drawing. Filed July 14, 1958, Ser. No. 748,150
Claims priority, application Germany July 16, 1957
12 Claims. (Cl. 260—666)

This invention relates to a process for the catalytic hydrogenation of carbocyclic compounds having olefinic double linkages. In particular, the invention relates to a process for the catalytic hydrogenation of carbocyclic compounds having olefinic double linkages which can be carried out on an industrial scale in a continuous manner.

It is known to hydrogenate carbocyclic compounds having olefinic double linkages at elevated temperature and under increased pressure in the presence of catalysts. By the said prior art methods, however, satisfactory yields on an industrial scale are only obtained when working in the liquid phase, for example by the trickling or sump methods, at very high pressures, as for example 100 to 300 atmospheres. Moreover, in the big-scale process for the perhydrogenation of the olefinic double linkages contained in carbocyclic compounds, the presence of a solvent is necessary, and the hydrogenation product must be separated therefrom by distillation.

A further general disadvantage of the known methods is the formation of isomeric byproducts which in unfavorable cases may be formed in amounts of 10 to 20%. These byproducts give rise to considerable difficulty in the distillative working up of the product, because the boiling points of the byproducts are insufficiently different from the boiling points of the main products.

We have now found that carbocyclic compounds having olefinic double linkages can be hydrogenated on an industrial scale and in almost quantitative yields by leading the initial material at raised temperature in the vapor phase with a large excess of hydrogen over a hydrogenation catalyst which is precipitated on a macroporous carrier.

According to the present invention, carbocyclic compounds having olefinic double linkages of the kind of cyclopolyolefines, i.e. cyclo-octatetraene or its higher homologes of the general formula $C_{2n}H_{2n}$, in which n represents 4 or a number greater than 4, for example cyclodecapentaene, cyclododecahexaene or vinylcyclooctatetraene and phenylbutadiene, can be hydrogenated. By the catalytic hydrogenation according to this invention, all the conjugated, cumulated or isolated olefinic double linkages contained in unsaturated compounds, whether in a ring or a chain or in both, are hydrogenated. On the contrary compounds which, like phenylbutadiene, contain an aromatic nucleus, are hydrogenated selectively only at their olefinic linkages, whereas the aromatic nucleus remains intact. From phenylbutadiene there is therefore formed, by hydrogenation according to this invention, phenylbutane. As initial materials for this hydrogenation, which can be carried out on an industrial scale, the carbocyclic compounds of the above-mentioned kind which have 8 to 12 carbon atoms in the molecule are especially important. It will be recognized that the term "olefinic double linkage" as employed herein refers to aliphatic unsaturation as distinct from aromatic unsaturation.

A special advantage of the process resides in the fact that it can be carried out at normal pressure but moderately increased or reduced pressures may also be used. It should be noted, however, that the process must be carried

out below the pressure at which with the working temperature chosen, liquefaction of the charging stock does not yet occur. The catalysts to be efficiently used in the hydrogenation in accordance with this invention are precious metals, such as platinum and palladium, and also all known mixed hydrogenation catalysts which contain nickel as the main constituent. When the catalysts are of the precious metal-type, they are used in amounts of 1 to 10% by weight, advantageously 3 to 7% by weight, with reference to the amount by weight of the carrier.

The mixed catalysts, above all nickel, copper and manganese catalysts, are used in amounts of 3 to 30% by weight, especially 10 to 25% by weight, with reference to the weight of the carrier. It has proved to be advantageous to use a nickel, copper, manganese catalysts which contains about 10 to 20% of nickel, 1 to 10% of copper and 0.5 to 5% of manganese with reference to the weight of the carrier.

It is of decisive importance for the success of the hydrogeneration that inert macroporous carriers should be used for the catalysts. By macroporous carriers we mean substances which have practically no micropores but also exclusively macropores. The pore diameter should not be less than 1000 A.=0.1 millimicron. The internal surface amounts to about 1 to 10 square meters per gram. Such catalysts carriers are for example:

Italian pumice (granulated):
Internal surface 1.2 square meters per gram
Micropore volume 0.012 cc. per gram
Macropore volume 1.124 cc. per gram
Mean pore radius 20,000 A.=2 millimicrons or
Kieselguhr:
Internal surface 5.58 square meters per gram
Micropore volume 0.011 cc. per gram
Macropore volume 1.836 cc. per gram
Mean pore radius 6,600 A.=0.66 millimicron.

Similarly catalyst carriers may be used which consist of precipitated or muffle-heated silica (mean pore radius=15,000 A.) and macroporous activated carbon.

By the use of these macroporous catalyst carriers in the gas phase hydrogenation according to this invention, for example of cyclo-octatetraene to cyclo-octane, the formation of bicyclo-(0.2.4)-octane by isomerization is avoided. In this way cyclo-octane is obtained in practically quantitative yield by the hydrogenation of cyclo-octatetraene.

The hydrogenation is preferably carried out in a continuous manner at temperatures of 120° to 300° C., preferably at 150° to 200° C. Space-time yields of 1.5 to 2.0 kilograms per liter of catalyst volume per day are reached.

For carrying out the process, the carbocyclic compound to be hydrogenated, for example cyclo-octatetraene, after vaporization in a suitable evaporation chamber, is led together with a multiple excess of hydrogen, for example with 10 to 50 times its amount of hydrogen, preferably at normal pressure, over the catalyst.

The following examples will further illustrate this invention but the invention is not restricted to these examples. The percentages are by weight, unless otherwise stated.

Example 1.

120 to 140 grams of cyclo-octatetraene vapor per hour are led together with hydrogen into a reactor which is filled with a hydrogenation catalyst consisting of 5% palladium on Italian pumice, the capacity of the reactor being 3 liters. The mixture of gas and vapor contains about 5% by volume of cyclo-octatetraene vapor. The hydrogen is circulated through the apparatus at normal pressure by means of a gas circulating pump and at the same time the temperature is kept constant at 150° to 160° C. The

hydrogen used up, about 25 liters per hour, is continuously replenished.

The circulating gas passed through a vaporizer in which cyclo-octatetraene is continuously vaporized at 150° to 180° C. and entrained by the current of hydrogen. After leaving the reactor, the mixture of hydrogen and cyclo-octane vapor is led through a gas cooler and the condensed cyclo-octane collected in a separator. The hydrogenation product has a freezing point of 8° to 10° C. when the cyclo-octatetraene used as initial material contains about 1% of styrene, 1% of benzene and 2% of phenylbutadiene. In the distillation, which is carried out at normal pressure, the cyclo-octane with a boiling point of 151° to 152° C. is obtained after a slight first runnings of ethylbenzene and benzene, and a small residue of phenylbutane remains in the flask.

The distilled cyclo-octane has a freezing point of 14.0° to 14.6° C.; the yield is almost quantitative.

Example 2

By carrying out the hydrogenation in the same way as described in Example 1 and using a hydrogenation catalyst consisting of 15% of nickel, 5% of copper and 1% of manganese on pumice granules, the same results are obtained.

Example 3

About 40 grams per hour of vinylcyclo-octatetraene in admixture with hydrogen are led into a reactor of 1 liter capacity which is filled with a hydrogenation catalyst (composition 12% of nickel, 3% of copper and 2% of manganese on kieselguhr). The gas-vapor mixture contains about 4% by volume of vinylcyclo-octatetraene vapor. The hydrogen is circulated through the apparatus at normal pressure with a blower and the reaction temperature is kept constant at 160° to 180° C. The hydrogen used up, about 8 to 10 liter per hour, is continuously replaced. The circulating gas is led through a vaporizer in which the vinylcyclo-octatetraene is continuously vaporized at 170° to 190° C. and entrained by the hydrogen. After leaving the reactor, the gas-vapor mixture is led through a gas cooler and the condensed ethylcyclo-octane collected in a separator. By distillation, which is carried out at normal pressure, the ethylcyclo-octane is obtained with the boiling point 188° C., after a small first runnings (about 5% of the total amount), while a small residue remains in the flask. The distillation product has a purity of 98%.

Example 4

50 grams per hour of a mixture of 60% of cyclo-octatetraene and 40% of (1)-phenylbutadiene-(1.3) are reacted in the apparatus described in Example 3. The vaporization temperature amounts to 160° to 180° C. The reactor itself is kept at a temperature of 160° to 170° C. A mixture of cyclo-octane and phenylbutane is obtained which is then distilled. At normal pressure, after a small first runnings, the cyclo-octane is obtained with a boiling point of 151° to 152° C. and then, after an intermediate runnings amounting to about 8% of the total amount, the phenylbutane is obtained with a boiling point of 180° to 181° C.

The yield of cyclo-octane amounts to 85 to 90% with reference to the cyclo-octatetraene contained in the initial mixture and the yield of phenylbutane amounts to 80 to 85% of the theoretical yield with reference to the phenylbutadiene contained in the initial mixture.

Example 5

80 to 100 grams of cyclododecatriene are hourly fed together with hydrogen into a reactor of 2 liters' capacity which is charged with a hydrogenation catalyst consisting of 12% of nickel, 2% of copper and 0.8% of manganese on Italian pumice. The gas-vapor mixture contains 4 to 6% by volume of cyclododecatriene vapor. The hydrogen is circulated through the apparatus at normal pressure with a gas circulation pump, the temperature in the reactor being thus kept constant at 240° to 250° C. The hydrogen used up, about 15 liters per hour, is continuously replenished.

The circulating gas passes through a vaporizer in which the cyclododecatriene is continuously vaporized at 245° to 255° C. and entrained by the current of hydrogen. After leaving the reactor, the mixture of hydrogen and cyclododecane vapor is led through a gas cooler and the condensed cyclododecane collected in a separator. The hydrogenation product has a freezing point of 45° to 50° C. and a cyclododecane content of about 98%. Besides it contains a small amount of unreacted cyclododecatriene.

We claim:

1. In a method of catalytically hydrogenating an olefinically-unsaturated hydrocarbon containing a carbocyclic group, the improvement which comprises carrying out said hydrogenation in the vapor phase at a temperature of from 120° C. to 300° C. and at substantially normal pressure with a large excess by volume of hydrogen in the presence of a hydrogenation catalyst which is deposited on a macroporous carrier having a pore diameter of not less than 1,000 A. and an internal surface area of about 1 to 10 square meters per gram.

2. An improved process as claimed in claim 1 wherein the hydrogenation catalyst is deposited upon a macroporous carrier selected from the group consisting of pumice, kieselguhr, silica and activated carbon.

3. An improved continuous catalytic hydrogenation process which comprises hydrogenating an unsaturated hydrocarbon selected from the group consisting of cyclooctatetraene, cyclodecapentaene, cyclododecahexaene, vinylcyclooctatetraene, phenylbutadiene and their partially aliphatically saturated homologous compounds in the vapor phase at a temperature of from 120° C. to 300° C. and at substantially normal pressure with a large excess by volume of hydrogen in the presence of a hydrogenation catalyst which is deposited on a macroporous carrier having a pore diameter of not less than 1,000 A. and an internal surface area of about 1 to 10 square meters per gram.

4. An improved process as claimed in claim 3 wherein said hydrogenation catalyst contains from 10 to 20% by weight of nickel, 1 to 10% by weight of copper and 0.5 to 5% by weight of manganese deposited on said macroporous carrier.

5. An improved process as claimed in claim 3 wherein the amount of hydrogen is about 10 to 50 times the amount of the unsaturated hydrocarbon.

6. An improved continuous catalytic hydrogenation process which comprises vaporizing an olefinically-unsaturated hydrocarbon containing a carbocyclic group, and leading the vapor together with an excess of about 10 to 50 times by volume of hydrogen at a temperature of between 120° C. and 300° C. and at about atmospheric pressure over a hydrogenation catalyst containing from 10 to 20% by weight of nickel, 1 to 10% by weight of copper and 0.5 to 5% by weight of manganese deposited on a macroporous carrier having a pore diameter of not less than 1,000 A. and an internal surface area of about 1 to 10 square meters per gram.

7. An improved process as claimed in claim 6 wherein the macroporous carrier is a member selected from the group consisting of pumice, kieselguhr, silica and activated carbon.

8. An improved continuous catalytic hydrogenation process which comprises vaporizing an unsaturated hydrocarbon selected from the group consisting of cyclooctatetraene, cyclodecapentaene, cyclododecahexaene, vinylcyclooctatetraene, phenylbutadiene and their partially aliphatically saturated homologous compounds, and leading the vapor together with an excess of about 10 to 50 times by volume of hydrogen at a temperature of between 120° C. and 300° C. and at about atmospheric pressure

over a hydrogenation catalyst containing from 10 to 20% by weight of nickel, 1 to 10% by weight of copper and 0.5 to 5% by weight of manganese deposited on a macroporous carrier selected from the group consisting of pumice, kieselguhr, silica and activated carbon, said carrier having a pore diameter of not less than 1,000 A. and an internal surface area of about 1 to 10 square meters per gram.

9. An improved process as claimed in claim 8 wherein the unsaturated hydrocarbon being hydrogenated is cyclooctatetraene.

10. An improved process as claimed in claim 8 wherein the unsaturated hydrocarbon being hydrogenated is vinylcyclooctatetraene.

11. An improved process as claimed in claim 8 wherein

the unsaturated hydrocarbon being hydrogenated is a mixture of cyclooctatetraene and phenylbutadiene.

12. An improved process as claimed in claim 3 wherein the hydrogenation is carried out at a temperature of from 150° C. to 200° C.

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