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DIMERISATION OF OLEFINES

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This invention relates to the dimerisation of olefines.

The dimerisation of butene-2 in the presence of an aluminium tri-alkyl and finely divided nickel at 100° to 250° C. and 50 to 500 atmospheres has been described.

We have now found that metals other than nickel which may be in the form of their reducible compounds, in association with an organo-compound of aluminium may be used in the dimerisation of butene-2 and other olefines not containing a terminal double bond. We have further found that this dimerisation process can be very effectively combined with subsequent carbonylation of the dimerisation product particularly when the metal employed in the dimerisation process is a carbonylation catalyst.

According to the presence invention there is provided a process for the dimerisation of olefines in which one or more olefines at least one of which does not contain a terminal double bond are brought into contact at elevated temperature and pressure with a reaction medium comprising an organo-compound of aluminium and a metal selected from copper and transition metals of groups 3 to 8 inclusive of the periodic system excluding nickel, or a reducible compound of the said metal.

The process of the invention is applicable to the dimerisation of a wide variety of olefines in which the double bond may have any position other than the terminal position. Examples of olefines which may be dimerised according to the process of the invention are butene-2, pentene-2 and heptene-3.

A mixture of olefines not containing a terminal double bond may be subjected to the dimerisation process and the resulting product may then contain dimers of the individual olefines and co-dimers. The mixture of olefines may also contain one or more alpha-olefines providing that at least one olefine in the mixture is an olefine not containing a terminal double bond. The alpha-olefine should contain the group —CH:CH_2. Examples of suitable mixtures of olefines are mixtures containing butene-2 and butene-1 and/or propylene.

The organo-compound of aluminium should be an aluminium hydride in which at least one of the hydrogen atoms is substituted by an alkyl, cyclo-alkyl or aryl radical. It is preferred to use an aluminium tri-alkyl such as for example, aluminium tri-ethyl, aluminium tripropyl and aluminium tributyl.

In forming the reaction medium the metal may be used in the elementary state or in the form of a compound, for example, a halide, which is at least partially reduced by the organo-compound of aluminium. The metal should be copper or a transition metal of groups 3 to 8 of the periodic system excluding nickel which catalyses the isomerisation of olefines.

Examples of suitable transition metals of groups 3 to 8 of the periodic system are titanium, chromium, iron and cobalt. We prefer that the metal is copper, iron or cobalt.

When the metal is used in the elementary state it should preferably be in a form which provides a large surface area e.g., in porous or fine'y divided form. The metal or reducible metal compound may be carried on a support such as for example kieselguhr.

While lower operating temperatures may be used for example, down to about 100° C., it is preferred that the

temperature is within the range 180° to 250° C. Temperatures higher than 250° C. may be used but such higher temperatures are usually unnecessary.

The process may be carried out under a wide range of pressures, suitably 50 to 400 atmospheres. Pressures in excess of 400 atmospheres may be employed but they are usually unnecessary. The particular pressure employed depends upon the operating temperature i.e. a higher pressure is desirable at the higher operating temperatures.

The reaction medium may also contain a solvent for the olefine which is inert under the reaction conditions. Paraffinic, saturated alicyclic and aromatic hydrocarbons are very suitable solvents.

The amounts of the organo-compound of aluminium and the metal or reducible metal compound employed may vary over a wide range. Suitable amounts are 1–30% organo-compound of aluminium and 0.01 to 5% metal which may be in the form of a reducible metal compound, by weight of the olefine.

The process may be operated batchwise or continuously. It is particularly adapted for continuous operation.

Water and oxygen should not be present in the apparatus in which the dimerisation is effected in more than trace amounts since they decompose organo-compounds of aluminium. Air is suitably displaced from the apparatus by an inert atmosphere of for example, nitrogen.

The process of the invention provides a product which may be carbonylated to form oxygenated compounds such as aldehydes and alcohols.

If the transition metal is a carbonylation catalyst, for example iron or cobalt, it is a particular further feature of the invention that the product of the dimerisation process may be carbonylated without separating the dimer or dimers from the reaction product. Intermediate separation steps are thus unnecessary and carbonylation may be effected without reduction of pressure, thereby avoiding a recompression step.

A unified process for the dimerisation of olefines and subsequent carbonylation of the dimerisation product is thus provided in which an intermediate separation step requiring reduction of pressure and subsequent recompression is avoided and in which the dimerisation product is carbonylated without further addition of a carbonylation catalyst.

Example 1

In experiments 1 to 5 butene-2 containing about 7% butene-1 was added to a suspension of 5 grams dry, finely powdered metal halide in a solution of 73 grams aluminium tripropyl in 125 grams decahydronaphthalene contained in a 1 litre chrome-steel rocking autoclave from which the air had been displaced by nitrogen. The contents of the autoclave were then heated at 200° C.

In order to demonstrate the effect of the metal halide, experiment 6 was carried out in the same way as experiments 1 to 5 except that a metal halide was not added to the aluminium alkyl solution which consisted of 29 grams aluminium tri-ethyl dissolved in 264 grams decahydronaphthalene.

The following table shows the weight of butene-2 used, the percentage conversion of butene-2 and the weight of dimer obtained. The dimer was isolated from the reaction product by distillation and it consisted mainly of 2-ethylhexene-1 together with smaller quantities of 2-methxylene-1 and 2-ethylpentene-1. These last two compounds were formed as a result of the presence of the propyl radical in the aluminium tripropyl.

Substantially no dimer of butene-2 was produced in ex-

periment 6, thereby demonstrating the considerable effect of the metal halide on the dimerisation of butene-2.

Experiment No.	Butene-2, gm.	Metal halide	Duration of experiment, hours	Percent conversion of butene-2	Dimer, gm.
1	300	$TiCl_3$	24	90	250
2	245	$CuCl_2$	24	94	200
3	242	$CoBr_2$	3	60	155
4	260	$FeCl_2$	6	59	117
5	261	$CrCl_2$	3	69	107
6	224	----------	3	<6	Nil

Example 2

260 grams butene-2 containing about 7% butene-1 was added to a suspension of 5 grams anhydrous, finely divided ferrous chloride in a solution of 83 ml. aluminum tripropyl in 125 grams cyclohexane contained in a 1-litre chrome-steel rocking autoclave from which air had been displaced by nitrogen. The contents of the autoclave were then heated at 250° C. for 3 hours.

The unchanged butene (51 grams) was then vented from the autoclave and a mixture of carbon monoxide and hydrogen in the ratio 3:2 introduced into the autoclave to maintain a pressure of 230 to 250 atmospheres with the temperature maintained at 160° C. After 12 hours the gas in the autoclave was replaced by hydrogen at the same pressure and the temperature maintained at 120° C. for 3 hours and then at 200° C. for 12 hours.

The reaction product was then discharged from the autoclave and hydrolysed with methanol; no gas was liberated. The aluminium alkoxides in the product were decomposed with dilute hydrochloric acid, and the organic liquid separated, dried and fractionally distilled at atmospheric pressure. The distillation products were cyclohexane, 25 grams 2-ethylhexene-1 and 133 grams of a mixture of alcohols including C_9 alcohols.

We claim:

1. A process for the dimerization of an olefine having from 4 to 7 carbon atoms and having the double bond in other than a terminal position which comprises contacting said olefine at a temperature above 100° C. and under elevated pressures with a reaction medium consisting essentially of aluminum trialkyl and a finely divided metal selected from the group consisting of copper and titanium.

2. The process of claim 1, wherein there is also present an alpha-olefin.

3. A process as claimed in claim 2 in which the alpha-olefine is selected from the group consisting of butene-1 and propylene and the olefine having the double bond in other than a terminal position is butene-2.

4. The process of claim 1, wherein said olefin is butene-2.

5. The process of claim 1, wherein said metal is introduced as a halide salt thereof, selected from the group consisting of chloride and bromide salts.

6. A process as claimed in claim 1 in which the temperature is maintained within the range 180° to 250° C.

7. A process as claimed in claim 1 in which the reaction medium also includes a solvent for the olefine which is inert under the conditions of the process.

8. A process as claimed in claim 7 in which the solvent is selected from the group consisting of paraffinic, saturated alicyclic and aromatic hydrocarbons.

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