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PREPARATION OF A β-OLEFIN FROM A STRAIGHT CHAIN TERMINAL OLEFIN WITH METALLIC MOLYBDENUM CATALYST

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ABSTRACT OF THE DISCLOSURE

A process for preparing β-olefins from α-olefins by contacting said α-olefins with a metallic moylbdenum containing catalyst. Molybdenum metal or a mixture of molybdenum metal and Group VIII metals are especially useful catalysts.

This invention relates to olefin isomerization and more particularly, to the isomerization of straight-chain terminal olefins to straight-chain internal olefins with a catalyst containing molybdenum alone or in admixture with Group VIII metal.

Various processes for isomerizing terminal olefins to internal olefins are known in the art. However, in general, the prior art processes suffer from one or more limitations such as excessive olefin cracking, undesirable olefin polymerization, excessive randomization, or unfavorable economics. It is known that palladium and platinum halides in combination with other ingredients can be employed as isomerization catalysts. U.S. Patent 2,960,550, Nov. 15, 1960, teaches the isomerization of olefins with a catalytic medium consisting essentially of a halogenated, straight-chain, organic acid solution of a halogen-containing salt of palladium or platinum. U.S. 2,960,551, Nov. 15, 1960, teaches similar catalytic media which consist essentially of a phosphorus oxychloride solutions of a halogen-containing palladium or platinum salt. In contrast, this invention comprises the discovery that halide salts of palladium and platinum are unnecessary, and that the isomerization of terminal olefins to internal olefins can take place in the presence of molybdenum or molybdenum admixed with one or more Group VIII metals. Furthermore, this invention comprises the discovery that halogenated reaction media such as halogenated straight-chain organic acids or phosphorus oxychlorides are unnecessary in the isomerization of terminal olefins.

An object of this invention is to provide a process for the isomerization of terminal olefins to internal olefins. A more particular object is to provide a process for the isomerization of straight-chain terminal olefins to straight-chain internal olefins which employs molybdenum as a catalyst. A further object is to provide an isomerization process which does not entail the use of a halogenated straight-chain organic acid or phosphorus oxychloride as an integral part of a catalytic system. Additional objects will be apparent from the following detailed description and appended claims.

The objects of this invention are accomplished by a process for the isomerization of an olefin which comprises contacting an olefin with a catalytic quantity of molybdenum metal alone or in admixture with one or more Group VIII metals. An embodiment of this invention is a process which comprises contacting an olefin with molybdenum alone or in admixture with one or more Group VIII metals. In a preferred embodiment, a straight-chain terminal olefin having from 4 to 24 carbon atoms is isomerized to a straight-chain internal olefin by contacting said olefin with a catalytic quantity of a catalyst consisting of molybdenum metal alone or in admixture with one or more Group VIII metals selected from the group consisting of palladium, platinum, rhodium, and ruthenium, and metal mixtures thereof; said metal or metal mixtures being dispersed on an inert support such as charcoal.

The process of this invention is advantageously employed in the conversion of straight-chain α-olefins having from 10 to about 28 carbon atoms to the corresponding straight-chain β-olefins. However, the process can also be used to isomerize lower olefins such as butene-1, pentene-1, hexene-1, octene-1, and the like. A particular feature of this invention is the high yield of β-olefin afforded by the process.

The reaction temperature is not critical. It is desired that the reaction temperature afford a reasonable rate of isomerization but not be so high as to produce an untoward decomposition of the starting olefin or internal olefin products. Thus, the temperature of from 20° C. to the decomposition temperature of olefin may be employed. Preferably the process is carried out at a temperature above about 100° C. Although temperatures as high as 300° C. or higher can be employed, it is usually desirable that the temperature be within the range of from about 150 to about 225° C. The latter range is a highly preferred temperature range for this process. In many instances, especially when isomerizing olefins such as dodecene-1, tetradecene-1, hexadecene-1, and the like, a convenient temperature is the reflux temperature of the system.

The pressure at which the process is conducted is not critical. Atmospheric pressure or lower or higher pressures can be employed. In some instances, when it is desirable to employ a reaction temperature above the normal boiling point of a material within the reaction mixture, it is desirable to use superatmospheric pressures. Thus, pressures as high as 10 or100 atmospheres or higher can be employed. A most preferred pressure range is from about ambient pressure to about 10 atmospheres.

The reaction time is not a truly independent variable but is at least dependent to some extent on the other process conditions employed. In particular, higher temperatures usually afford a faster reaction time while, on the other hand, lower reaction temperatures tend to increase the time necessary for reaction. Furthermore, the reaction time depends to some extent on the amount of catalyst used for a given volume of olefin and to some extent on the specific metal mixture employed as the catalyst. When carrying out the process as a batch operation, reaction times within the order of from about 10 minutes to about 20 hours are usually sufficient.

The amount of catalyst employed in this process is not critical. However, it is preferred that an amount of catalyst be used which affords a reasonable amount of isomerization in a reasonable reaction time. In general, when the process of this invention is carried out as a batch operation, from about 0.01 to about 40 weight percent of a catalyst is employed, said catalyst consisting of from 0.1 to about 50 percent molybdenum or a mixture of molybdenum and at least one other metal from Group VIII and the remainder an inert support. A preferred range is from about one to about 15 weight percent. Thus, for example, if 100 grams of olefin is charged to the reaction vessel, it is highly preferred that from about one to about 15 grams of a catalyst mixture, that is, a mixture of the metals and the inert support, be admixed therewith.

As mentioned above, the metal content of the catalyst may be either molybdenum alone or molybdenum in admixture with one or more of Group VIII metals, preferably in a finely divided state. Metal alone may be used as the catalyst or it may be used in conjunction with a

relatively inert support. In the latter instance, the metal may be dispersed on a catalytic support. Suitable supports which may be employed include charcoal, alumina, diatomaceous earth, bentonite, firebrick, kaolin, ground glass, silicon carbide, silicon dioxide, kieselguhr, and the like. The catalyst may be employed in a finely divided form. Similarly, it can be used in particular forms such as pellets, tablets, etc. In addition, this catalyst may be dispersed on a metal or ceramic screen. Charcoal, and particularly finely divided charcoal, is the preferred inert support.

The molybdenum catalysts of this invention may be prepared by any conventional methods employed in the catalyst art which produce materials having high surface area. For the purpose of illustration, some of the methods which may be used to yield molybdenum in the desired state are reduction of molybdenum oxides and decomposition of molybdenum chloride or molybdenum carbonyls. Other known methods include the use of molybdenum-aluminum alloys which, when treated with an alkali, will yield molybdenum with high surface area, and the use of molybdenum-amalgam which, after removal of mercury, produce pyrophoric molybdenum. Since the method of preparing the catalyst is not critical, any known method may be employed.

The process of this invention is carried out by contacting the olefin to be isomerized with the catalyst. It is not necessary to include other ingredients within the reaction zone. However, in some instances it is desirable to do so. For example, under certain circumstances it may be desirable to isomerize under an inert atmosphere. In addition, solvents which are inert under the process conditions employed can be used in this process. Typical solvents of this type are paraffinic materials such as hexane, dodecane, and mixtures thereof such as ligroin, kerosene, No. 9 oil, and the like.

The process of this invention may be carried out in air or in an inert atmosphere. When it is desired to use an inert atmosphere, nitrogen is the gas of choice for economical reasons. However, other inert gases such as neon, argon, krypton and the like can be employed if desired.

The process of this invention can be carried out as a batch process or as a continuous operation. In a continuous process, an olefin, either in vapor or in liquid phase, may be contacted with the catalyst, but for practical reasons, liquid phase operations are preferred. When carrying out the process of this invention as a batch operation, it is preferred that a liquid phase be present. Thus, dodecene-1 can be isomerized by refluxing a mixture of dodecene-1 and catalyst at atmospheric pressure. Similarly, butene-1 can be isomerized in batch operation by contacting it with a catalyst at a pressure under which the terminal olefin is a liquid. Alternatively, butene-1 (or any terminal olefin that is gaseous at the reaction temperature) can be isomerized according to the process of this invention by bubbling the gaseous olefin through a liquid reaction medium containing the catalyst.

When this process is carried out using olefin vapors and a continuous process, an inert gas, preferably nitrogen, is advantageously used as a carrier for the olefin that is being passed through the catalyst bed. In such a process the amount of nitrogen used as compared to the amount of olefin should be such that the volume of nitrogen to olefin be within the range of 1:1 to 1000:1.

In a continuous process, occasionally a single pass of an olefin through the reaction column might not yield the desired degree of isomerization. In such cases, the partially isomerized olefin may be recycled in the same manner as the fresh olefin through the reaction column to produce the desired degree of isomerization.

When the process of this invention is a continuous process, an additional variable of space velocity is introduced. Space velocity may be defined by the following relationship:

$$\text{Space velocity (s.v.)} = \frac{\text{ml. olefin injected/ml. catalyst}}{\text{hours}}$$

The above formula for calculating space velocity holds whether the olefin employed is in liquid or gas phase. The value for space velocity, however, will be substantially different when the olefin is in one or the other physical state. For example, when the olefin is in a liquid state, space velocity generally is in the range of from 0.1 to about 100, and more preferably, from 0.5 to about 10. On the other hand, when the olefin is in a gaseous state, space velocity is in the range of from about 50 to about 500. The reason for difference in the values for space velocity is that there is substantially much less olefin in each milliliter of olefin in gaseous state than in each milliliter of olefin in a liquid state.

Space velocity is thus a measure of the speed with which an olefin is passed through the reaction tube containing the catalyst bed. Space velocity in a continuous process, similarly as the reaction time in a batch process, is not a directly independent variable. It depends on the reaction temperature, the activity of a particular catalyst employed, and the degree of isomerization desired. It will be seen then that in order to achieve a given amount of isomerization, the space velocity generally will be different for different catalysts even if all other variables remain constant.

From the above discussion, it is clear that for optimum results the space velocity and the nitrogen flow must be determined for every isomerization when a different catalyst or a different olefin is employed. Not only the activity of the catalyst and the reaction temperature must be considered, but also the degree of isomerization desired, since, generally, the higher the degree of isomerization, the more time is required to attain it. Generally speaking, however, space velocity for liquid olefins will be in the range of from 0.1 to about 100, and preferably from 0.5 to about 10, and for gaseous olefins from about 50 to about 500.

As pointed out above, the process of this invention is particularly useful in the isomerization of α-olefins having from 10 to 28 carbon atoms. Illustrative but non-limiting examples of olefins of this type include decene-1, dodecene-1, hexadecene-1, octadecene-1, eicosene-1, docosene-1, pentacosene-1, octacosene-1, and the like. It is preferred that these olefins be straight-chain olefins. In other words, materials like n-hexadecene-1, n-docosene-1, and the like be isomerized by this process. Similarly, the normal or straight-chain isomers of the olefins above mentioned are also preferred starting materials. If desired, mixtures of olefins may be isomerized by this process.

The products of this invention can be separated from the reaction mixture by any method known in the art. Suitable separation techniques include distillation, adsorption chromatography, gas chromatography, and the like.

The following examples serve to illustrate the process of this invention but do not limit it. All parts are by weight unless otherwise noted.

EXAMPLE 1

A flask equipped with a side arm fitted with a diaphragm is charged with 100 parts of n-dodecene-1 and one part of a catalyst consisting of 10 percent molybdenum dispersed on charcoal. The flask is swept with nitrogen and after heating the reaction mixture to reflux for 8 hours, the product is found to contain a high yield of β-olefin.

EXAMPLE 2

The procedure of Example 1 is repeated except that 10 parts of the catalyst is employed and the reflux time is four hours.

EXAMPLE 3

The procedure of Example 2 is repeated except that the olefin employed is n-tetradecene-1, yielding n-tetradecene-2.

Similar results are obtained when molybdenum alone is used in amounts of from 0.1 weight percent to about 15 weight percent, based on the amount of olefin or when the olefin employed is n-decene-1, n-hexadecene-1, n-eicosene-1, or n-tetraeicosene-1, producing corresponding β-olefins.

EXAMPLE 4

A reaction vessel equipped with a side arm is charged with 100 parts of n-dodecene-1 and 10 parts of a catalyst consisting of 9 percent molybdenum and one percent ruthenium dispersed on charcoal. The reaction flask is swept with nitrogen and the reaction mixture heated to reflux for three hours. The product, n-dodecene-2, is obtained in high yield.

EXAMPLE 5

The procedure of Example 4 is repeated except that the catalyst consists of one percent molybdenum and nine percent ruthenium dispersed on charcoal.

EXAMPLE 6

The procedure of Example 4 is repeated except that five parts of catalyst is employed, said catalyst consisting of 5 percent molybdenum and 5 percent ruthenium dispersed on charcoal. The reflux time is about two hours.

Similar results are obtained when Examples 4, 5, and 6 are repeated substituting n-decene-1, n-hexadecene-1, n-eicosenene-1, and n-tetraeicosene-1, for dodecene in said examples, yielding corresponding β-olefins.

EXAMPLE 7

A flask equipped with a side arm is charged with 100 parts of n-tetradecene-1 and 10 parts of a catalyst consisting of 20 percent molybdenum and 10 percent palladium dispersed on charcoal. The reaction flask is swept with nitrogen and heated to reflux for one hour after which the product is found to contain a high yield of n-tetradecene-2.

EXAMPLE 8

The procedure of Example 7 is repeated except that 15 parts catalyst comprised of 10 percent molybdenum and 40 percent palladium dispersed on charcoal is employed.

EXAMPLE 9

The procedure of Example 7 is employed except that one part of the catalyst composed of 25 percent molybdenum and 25 percent platinum dispersed on charcoal is employed. The reflux time is seven hours.

EXAMPLE 10

The procedure of Example 7 is repeated except that the catalyst is composed of 2.5 percent molybdenum and 7.5 percent rhodium dispersed on charcoal. The reflux time is 2.5 hours.

When n-decene-1, n-hexadecene-1, n-eicosene-1, n-tetraeicosene-1, n-octaeicosene-1, 5-methyldodecene-1, and 2-methyldodecene-1 are employed in place of n-tetradecene-1 in Examples 7–10, high yield of corresponding β-olefins are obtained.

The process of this invention may also be extended to the Group VIB metals such as chromium and tungsten alone or in admixture with molybdenum and/or Group VIII metals.

The internal olefins produced by the process of this invention are well-known compounds and have the many utilities which are known for them. For example, they are valuable chemical intermediates and can be transformed into acids by an ozonolysis reaction. Thus, for example, tetradecene-2 can be reacted with ozone to yield lauric acid, a detergent range acid. Similarly, the other internal olefins produced by this process can be ozonized to yield the corresponding acids. When ozonizing the products of the process of this invention, the reaction is generally carried out at a low temperature; e.g., from −50 to about 10° C. After the ozonization reaction is completed, the resultant reaction mixture is usually treated with another oxidant such as air or oxygen to obtain the product acid. The secondary oxidation is usually carried out at a temperature within the range of 20 to 90° C. Solvents which can be employed in the ozonolysis of olefins include inert solvents such as chloroform and carbon tetrachloride or hydroxylic solvents such as methanol and acetic acid.

Having fully described the process of this invention, the products produced thereby and their many utilities, it is desired that this invention be limited only by the lawful scope of the appended claims.

We claim:

1. A process for the preparation of a β-olefin, said process comprising contacting a straight-chain terminal olefin having from 4 to 28 carbon atoms with from 0.01 to 40 weight percent of a catalyst, said catalyst consisting essentially of metallic molybdenum dispersed on a relatively inert support such that said catalyst contains from 0.1 to 50 weight percent molybdenum; said process being conducted at a temperature of from about 100 to about 300° C. and at a pressure within the range of from atmospheric pressure to 100 atmospheres.

2. The process of claim 1 wherein said relatively inert support is finely divided charcoal.

3. A process for isomerizing a straight chain teminal olefin having from 4 to about 28 carbon atoms to a straight chain β-olefin, said olefin comprising contacting said terminal olefin with from 0.01 to 40 weight percent of an isomerization catalyst, said catalyst consisting essentially of a metallic component dispersed on finely divided charcoal, said metallic component being selected from the class consisting of molybdenum admixed with an additional metal selected from the group consisting of palladium, platinum, rhodium, iridium, and ruthenium such that the weight ratio of molybdenum to said additional metal is within the range of from 9 to 1 to 1 to 9, and such that the metallic content of said catalyst is from about 0.1 to about 50 weight percent, said process being conducted at a temperature of from about 100° to about 300° C. and at a pressure of from about atmospheric pressure to about 100 atmospheres.

4. The process of claim 3 wherein said catalyst is employed in the amount of from about one to about 15 weight percent of said olefin.

References Cited

UNITED STATES PATENTS

2,690,433	9/1954	Engel et al.	252—470
2,963,449	12/1960	Nixon	252—470
2,608,534	8/1952	Fleck	260—683.2
2,739,133	3/1956	Schwarzenbek	252—467
2,982,741	5/1961	Cleaver	252—467
3,052,739	9/1962	Hummers	252—467
3,117,097	1/1964	Janoski	252—467

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