This invention relates to the dimerization of olefins. One object of this invention is a method for dimerizing organic hydrocarbons having more than two carbon atoms in their molecule. This and still further objects will become apparent from the following description:

According to the invention, unsaturated organic hydrocarbons containing more than two carbon atoms in their molecules, or mixtures of these unsaturated hydrocarbons, are dimerized by heating such hydrocarbons to a temperature of about 50 to 250° C in the presence of hydrides or certain organo compounds of aluminium or its next highest group members in the periodic system, i.e., gallium and indium or its adjacent group member beryllium, which act as exceptionally effective agents for forming dimers of these hydrocarbons.

These new dimerization activators have the general formula Me(R), in which Me is one of the aforementioned metals, i.e., aluminium, gallium, indium or beryllium, n is the valence of the metal, and R is at least one of hydrogen, monovalent saturated aliphatic radicals, monovalent aromatic organic radicals or any compounds thereof. Suitable activators according to the invention are, for example: Be(C₂H₅)₂, H₂Al, H₂Al(C₂H₅), H₂Al(C₃H₇), H₂AlCl₂, Al(CH₃)₂, Al(C₂H₅)₂, Al(C₃H₇)₂, Ga(C₂H₅), In(C₂H₅), Be(C₂H₅), Al(CH₃), Al(C₂H₅), Ga(C₂H₅), In(C₂H₅), and the like.

These new dimerization activators may also be present in the form of their known, and in many cases very stable, organic molecular compounds with, for instance, ethers, thioketones or amines, or else in complex linkage with alkaline metal hydrides, alkyls or aryls. Examples of the activator compounds are: Na(Al(C₂H₅)₃), LiAlH₄, LiAl(Al(C₂H₅), NaAl(C₂H₅)₄, and the like.

The dimerization, according to the invention, is carried out at a temperature of about 80 to 250° C. The reaction may be carried out at normal pressures or increased pressures up to the highest possible pressures, as, for example, pressures of 2,000 atmospheres or still higher, as may be practically obtained in present operations. The activators in accordance with the invention may not be true catalysts in the scientifically strict meaning of the word, as they do not remain during the reaction exactly the same as they were when originally added. They may be present in small non-stoichiometrical quantities and still bring about comparatively large conversions. The activators form compounds with the olefins and such compounds are frequently contained as by-products in the reaction products. When the expression "dimerization" is used herein and in the claims, there is meant thereby the formation of a dimer of two unlike unsaturated hydrocarbon molecules, as well as the formation of a dimer of two like molecules of unsaturated hydrocarbon.

Any unsaturated hydrocarbons which have more than two carbon atoms in the molecule may be used to form the dimers in accordance with the invention. A single unsaturated hydrocarbon may form a dimer with itself, or two different unsaturated hydrocarbons may be dimerized. Olefins which have a terminal double bond, and olefins having in the intermediate position may be used in accordance with the invention.

The higher olefins may be used in accordance with the invention, and it has been found that alpha olefins react more rapidly than olefins which have the double bond in the intermediate position. There is, however, no fundamental difference with regard to the reaction products obtained. Thus, for example, in the case of heptene-(1) and heptene-(3) the dimeric heptenes produced are identical.

This is due to the fact that the double bond is able to migrate under the influence of the organo metal activators. From heptene-(3), for example, heptene-(1) may be produced at times in accordance with the invention and this heptene-(1) will form the dimer.

In addition to the dimers, polymers may also be formed. The formation of a dimer, however, is strongly preferred. Thickey viscous polymeric reaction products may be obtained in addition to the dimers in a ratio of 1:1 in certain cases, as for example with the use of heptene-(3), if heating is effected for comparatively long periods of time.

The method, according to the invention, is by no means limited to olefins of relatively low molecular weight. It is possible to, for example, convert dodecene in accordance with the invention.

Example 1

Al(C₂H₅)₃ was diluted with 10 times its volume of pentane. To this was added 30 times its weight of propylene. The mixture was made in an autoclave and heated at a temperature of 180° C. at a pressure of 170 atmospheres. The pressure was noted to drop to 40 atmospheres within a few hours. Additional propylene was added under pressure, and the reaction started again. The reaction was continued in this manner until the autoclave was completely filled with the reaction products. These reaction products contained a small initial amount of hydrocarbons of the C₆ and C₇ series. About 70% of the propylene was dimerized into 1-methyl-1-propyl-ethylene.

OCH₃
C=CH₃
OCH₃
and which boiled at 65° C. and had an n₀=1.3920. In addition to these reaction products, a few parts per 100 of trimercap propylene and higher polymers were also obtained.

Example 2

The procedure used in Example 1, using Al(CH₃)₃, was followed and the identical 1-methyl-1-propyl-ethylene was obtained.

The dimers formed, in accordance with the invention, when a single unsaturated hydrocarbon is used, will be of the general formula (dimerized hydrocarbon)₂. When two different unsaturated hydrocarbons are dimerized in accordance with the invention, as, for example, hydrocarbon, hydrocarbons, then the dimers produced in accordance with the invention will consist of (hydrocarbon)₂ plus (hydrocarbon₁ plus hydrocarbons) plus (hydrocarbons)₂.

Example 3

Pure propylene freed from oxygen and moisture is used. 1-2% of aluminium trimethyl Al(CH₃)₃ by weight of the propylene is added to the propylene in an autoclave, while the propylene is under pressure, but still in gaseous phase. The temperature is then raised to 200° C, whereupon the pressure increases to about 170 atmospheres. After several hours the pressure has increased to about 30-40 atmospheres, whereupon new propylene may be again pressed into the autoclave, thereby repeating the reaction until the autoclave is substantially filled with the propylene conversion product. Pressure is then released and the autoclave is opened. Colorless, readily movable liquid is obtained, which, upon distillation, shows at least 70-80% of the used propylene in the form of a liquid having a constant boiling point of 65° C., and essentially representing 1-methyl-1-propyl-ethylene [2-methyl-pentene-(1)].

CH₃
C=CH₃
CH₃.OH.OH.C₂H₅
Analysis shows that the hydrocarbon is very pure and
that the same is substantially free from any isomers having a differently positioned double linkage such as for instance the isomer represented by the formula. In addition, the distillation residue contains small amounts of a trimer propylene as well as still higher boiling constituents of only consistency.

Example 4

Example 1 was repeated using the same conditions and materials as they are set forth, except that respectively 

Al(C₄H₇)₃, Al(C₅H₇)₃, and Al(C₆H₅)₃ were substituted for the aluminum trimethyl there prescribed. Essentially the same reaction products were obtained as set forth in the preceding example.

The dimerization velocity of the propylene increases rapidly with the amount of the initial added metal-organic compound. Thus, when using about 10–20% of aluminum triakyl in the propylene, the reaction velocity is so high that the same may be advantageously utilized for effecting continuous operations. When proceeding in this manner the solution of the activator in propylene under pressure is permitted to pass from the tap into a heated reaction chamber or alternatively into a tubular coil heated to about 200–240°C. At the lower end of which there is recovered a solution of the metallo-organic activator and dimer propylene together with unused propylene. Components may be easily separated by distillation. Propylene and recovered activator material are recycled into the process. The activator remains effective for a long period of time and despite the relatively large addition of 10–20% activator material initially used, the account of such activator material continuously required for the replenishment of activator material loss is relatively small in relation to the yields of variantly dimers obtained.

All α-olefins of the formula C₆H₄₊₁.CH=CH₂ reacts similarly to propylene. They can all be converted under the same conditions into dimer products of the general formula.

C₆H₄₊₁.CH=CH₂ → C₆H₄₊₁.CH⁻₂H₂

There are always, however, obtained by way of by-products certain amounts of isomers of the initially used olefins with differently positioned double linkages. Proceeding from butene-(1) preponderantly dimer butene

C₃H₆ → C₂H₆

of a B. P. of 118° is obtained, but also butene-(2). Proceeding from pentene-(1) preponderantly dimer pentene

C₅H₁₀ → C₄H₈

of a B. P. of 118° is obtained, but also butene-(2). Proceeding from hexene-(1) preponderantly dimer hexene

C₆H₁₂ → C₅H₁₀

of a B. P. of 164° (14 mm.) is obtained, but also a mixture of hexene-(2) and hexene-(3). Starting with dodecene-(1) large amounts of dimer dodecene

C₁₅H₃₀ → C₁₄H₂₈

of a B. P. of 155–160° (0.001 mm.) are obtained, but also various isomer dodecenes, varying with the position of their double linkages at the C atom positions of 2, 3, 4, 5 and 6. Such olefin or olefin mixtures with the intermediate double linkages are not directly obtained in the dimerization discussed above. These, however, do have the characteristic that when in contact with the metallo-organic activators a shifting of the double linkage will occur. Thus, similar to the shifting of the double linkage occurring as a side reaction to the dimerization of, for instance, hexene as shown in formula

CH₃.CH₂.CH₂.CH=CH₂ → CH₃.CH₂.CH₂.CH⁻₂H₂

the reverse is possible for olefins with intermediate double linkage. Within the conditions of operation the following equilibrium is obtained:

CH₃.CH₂.CH₃.H.CH=CH₂ → CH₃.CH₂.CH₂.CH⁻₂H₂ → CH₃.CH₂.CH₃.H.CH⁻₂H₂

This has the effect that not only α-olefins, but also isomer compounds with other α-positioned double linkages are finally converted to a very large extent when heated in the presence of the aforementioned dimerization activators to form the dimers of the corresponding α-olefins. This, however, will require a longer period of time than is necessary when subjecting the same isomer directly to the dimerization reaction. The dimerization of the pure pentene-(2) into the decene of the formula

C₁₀H₂₀ → C₉H₁₈

requires for instance under otherwise the same reaction conditions a five times greater reaction period than is necessitated by the conversion of pentene-(1) into the identical decene.

It is thus clear that the dimerization of olefins proceeds in accordance with two clearly identifiable phases. At first the principal amount of the α-olefin reacts rapidly, forming dimerization products. At the same time, as indicated above, the equilibrium mixture of the corresponding olefins with intermediate double linkages is formed in a side reaction. This will finally also become dimerized though requiring a much longer period of time. These differential reaction velocities may, on the other hand, also be utilized to remove by dimerization reaction α-olefins from a mixture of α-olefins with the less reactive olefins of intermediate double linkages.

The velocity of the dimerization of pure α-olefins is, independent of the size of the molecule, always approximately the same magnitude. This is true even though this velocity in normal cases decreases with increasing molecular weight. This is so because the concentration of the unsaturated end grouping decreases in the liquid olefin with increasing molecular weight. It has not been possible to establish any limit to the dimerization capacity. Even octadecene-(1) may be readily converted into a dimer which probably corresponds to the formula

C₂₀H₄₀ → C₁₉H₃₈

The scope of application of the new method to olefins with intermediate double linkage is, however, more limited. When in equilibrium, the proportion of α-olefin in the mixture constantly decreases with increasing length of the olefins, because of the increasing number of possible products. For this reason the reaction velocity of these olefins decreases rapidly with increasing chain length and finally approaches a limit beyond which dimerization can no longer be accomplished within any practically useful time periods. This limit is approximately olefins with about 12 carbon atoms in the chain.

The olefins useful for the dimerization in accordance with the present method need not be exclusively of the straight chain type. Also branched chain hydrocarbons such as

CH₃

CH⁻₂H₂

and aralkyl hydrocarbons such as

CH₃.CH₂.CH₃.CH₂.CH₃.CH₂.CH₃.CH₂.CH₃.CH₂.CH₃.CH₂.CH₃.CH₂.CH₃.CH₂.CH₃.CH₂.CH₃.CH₂.CH₃.CH₂.CH₃.CH₂.CH₃.CH₂.CH₃.CH₂.CH₃.CH₂.CH₃.CH₂.CH₃.CH₂.CH₃.CH₂.CH₃.CH₂.CH₃.CH₃
may be dimerized in accordance with the invention. It is further possible to effect mixed dimerization of two different olefins. When thus heating, for instance, under the conditions above described, a mixture of propylene and α-butyne with several percent of aluminum alkyl at a temperature of 200° C. or with aluminum hydride for several hours at 70-80° C., followed by heating to 200-220° C., an excellent yield of a colorless liquid is obtained which, upon distillation, in an efficient column produces approximately equal proportions of the following hydrocarbons

\[
\begin{align*}
\text{CH}_2 &= \text{CH}_2 \\
\text{CH}_3 &= \text{CH}_2 \\
\text{CH}_3 &= \text{CH}-
\end{align*}
\]

In a similar manner dimerization may be effected between propylene and hexene, pentene and heptene, butene with dodecene, etc., the number of such combinations being practically unlimited.

It is a disadvantage of the last-described method that the same always produces mixtures of products of ordinary dimerization with products of mixed dimerization. It is, however, possible to control these reactions, leading them along predetermined directions. This may be accomplished, for instance, by the following artificial: aluminum trialkyl is used as the activator material, using as the alkyl component one of the same C number as one of the two olefin components. Thus, for instance, aluminum tributyl is used when it is intended to combine butene-(1) and propylene. The aluminum tributyl is then heated with 3 mols of propylene (under pressure) to a temperature of 130-150° C., whereby the propylene disappears, being taken up by the tributyl aluminum to form an intermediate compound. If the latter is then heated under pressure to the same temperature with α-butyine disappearance or at least substantial disappearance of the butylene occurring, the aluminum tributyl is reformed and predominantly 1-butyne-1-methyl ethylene

\[
\begin{align*}
\text{C}_3\text{H}_4 &= \text{C} = \text{CH}_2 \\
\text{C}_3\text{H}_5 &= \text{C} = \text{CH}_2 \\
\text{C}_3\text{H}_5 &= \text{C} = \text{CH}_2
\end{align*}
\]

and

\[
\begin{align*}
\text{C}_3\text{H}_5 &= \text{C} = \text{CH}_2 \\
\text{C}_3\text{H}_5 &= \text{C} = \text{CH}_2 \\
\text{C}_3\text{H}_5 &= \text{C} = \text{CH}_2
\end{align*}
\]

Example 5

Dodecane was mixed with 4% Al(C₂H₅)₃ etherate and heated for 16 hours at 230° C. At the end of this time a dimer was recovered having a boiling point of 155° C. at 0.1 mm. The dimer formed was determined to have the following equation:

\[
\begin{align*}
\text{C}_6\text{H}_{12} &\text{C} = \text{CH}_2 \\
\text{C}_6\text{H}_{12} &\text{C} = \text{CH}_2
\end{align*}
\]

Example 6

2 cc. of beryllium and 63 grams of propylene are heated in an autoclave of about 200 cc. contents to about 80° C. to 110° C. while in a nitrogen atmosphere. The pressure at first increased to about 15 atmospheres and then decreased to about 9 atmospheres. From the autoclave contents it was possible to obtain by distillation 52 grams of 2-methylpentene-(1).

Example 7

100 kg. of liquid propylene were mixed in a pressure container with 10 kg. of aluminum tripropyl and were then passed through a tubular coil heated to a temperature from 200° C. to 210° C. The tubular coil was provided at its lower end with a pressure release valve and the lower end of the tubular coil was cooled. The valve terminates in a container filled with nitrogen. The propylene Al(C₃H₅)₃ mixture is pressed through the heated tubular coil at such velocity that the period of its remaining within the heated zone is from one half to two hours. When proceeding in this manner, there is continuously obtained a mixture of from 70 to 90 parts of 2-methylpentene-(1) with some unchanged propylene as well as small portions of higher polymer products the same containing additionally the aluminum organo compounds by way of dissolution in the distilled over products. The hydrocarbons may be separated by distillation and the distillation residue is again mixed with 100 kg. of propylene and the operation is repeated as above set forth. It is possible to dimerize in this manner at least 1000 kg. of propylene in a substantially continuous manner since the aluminum organic liquid contact material retains its effectiveness for a long period of time. When the effectiveness of the contact material becomes im-
paired, it is of advantage to distill the same in vacuum or and preferably a fairly high vacuum to thereby free the same from the difficulty volatilizable components. If necessary, the contact material may be replenished by the addition of fresh aluminum tripropyl.

**Example 8**

1 kg. of pentene-(1) and 50 grams of Al(CH₃)₃ are heated in an autoclave of about 5 liters content under exclusion of air to a temperature of about 200° C. The pressure rises temporarily to about 33 atmospheres and thereupon decreases during a period of about 15 hours down to about 12 atmospheres. After cooling, the autoclave content being substantially liquid, is washed with diluted hydrochloric acid to free the same from aluminum, whereupon the same is dried and distilled. In this manner there is obtained in addition to some unchanged pentene a total of about 890 grams polymer product, of which about 700 grams have a constant boiling point of about 164° C. and which demonstrate upon closer analysis to be substantially pure 2-propylpentene (1)

\[
\text{C}_6\text{H}_{13} \quad \text{C}_6\text{H}_{13}
\]

When repeating this example except that pentene-(2) is used, it is necessary to heat for a longer period of time until the pressure decrease is obtained. In all other respects, however, the same results are obtained and the same conditions prevail. In that case, however, the amount of the higher molecular products remaining in the distillation residue is somewhat larger. Mixtures of pentene-(1) and pentene-(2) give analogous results.

**Example 9**

440 grams of propylene and 720 grams of pentene-(1) both completely dry and free from air are admixed with 10 grams of solid aluminum hydride from which its ether content has been previously removed to the maximum possible extent (of about 95% ether) by careful keeping at a relatively high vacuum. The mixture is heated in an autoclave at first for a period of about 2 hours to a temperature of about 70° C. and is thereafter heated for 15 hours at a temperature of about 210° C. Thereafter the substantially liquid autoclave content is washed with diluted hydrochloric acid and is then carefully distilled. There were obtained when proceeding in accordance with this example 40 grams of propylene, 90 grams of pentene, 150 grams of pure 2-methylpentene-(1) of boiling point 63° C., 400 grams of a hydrocarbon of the Cs series of a boiling point of about 118–119° C. and 200 grams of substantially pure 2-propylpentene-(1) of a boiling point of about 167° C. In addition, intermediate fractions were obtained which upon separation yielded further products of the above named products.

The hydrocarbon of the Cs series yields upon cleavage with ozone a mixture of ketones of the composition C₆H₄O which upon analysis proved to be a mixture of about equal parts of methylyketones and dipropylketone of the respective formulae

\[
\text{C}_6\text{H}_{13} \quad \text{C}_6\text{H}_{13}
\]

The Cs hydrocarbon may thus be expected to contain the two components

\[
\text{C}_6\text{H}_{13} \quad \text{C}_6\text{H}_{13}
\]

In all of the foregoing examples there may be used in lieu of the activators specifically therein referred to any other of the activators within the general group definitions herein set forth and especially those for particularly good results herein specifically set forth. The purest products are, however, always obtained when proceeding with the dimerization of the olefins in accordance with the invention utilizing for the activator alkyl radicals of the same carbon number as they are used in the olefin. Similarly the purest products are also then obtained when within a preferred embodiment of the invention aluminum hydride or beryllium hydride are used. These are, however, only refinements and are not as such absolutely necessary. Thus, for instance, it is readily possible to substitute for the Al(CH₃)₃ of Examples 1 and 8 the equivalent amount of any of the following:

\[
\text{Al(CH₃)₃, Al(CHR)₃, AlH(CH₃)₂, H₂Al(CH₃)₂, CH₃Al, CH₃H, CH₃H, CH₃H, \text{ etc.}}
\]

No material changes are otherwise necessary when using these substitute activators in the reaction or procedures referred to and the results obtained, as well as the reaction conditions are substantially the same as those described in the hereinbefore referred to examples.

Though any of the other activator compounds herein referred to and usable within the scope of our invention give good results, the triethylaluminum (Al(CH₃)₃) is the preferred activator material because the same is the most readily available at this time and therefore lends itself best to practical use in commercial applications. It is, of course, obvious that many embodiments and dimerization of many different unsaturated hydrocarbons may be made in accordance with the invention. The invention is, therefore, in no way intended to be limited by the terms and the examples, being limited only by the appended claims or their equivalents.

1. Method for dimerizing unsaturated straight-chain hydrocarbons containing more than two carbon atoms in the molecule, which comprises heating such hydrocarbons at a temperature of about 80 to 250° C. in the presence of a dimerization activator having the general formula Me(R)ₙ in which Me is one metal selected from the group consisting of beryllium, aluminum, gallium and indium; R is at least one substituent selected from the group consisting of hydrogen, monovalent saturated aliphatic hydrocarbon radicals, and monovalent aromatic hydrocarbon radicals; and n is the valence of the metal Me, and recovering a dimer.

2. Method according to claim 1 in which said unsaturated hydrocarbons consist of a single unsaturated hydrocarbon.

3. Method according to claim 1 in which said unsaturated hydrocarbons are a mixture of at least two different unsaturated hydrocarbons.

4. Method according to claim 1 in which said hydrocarbons are olefins having an intermediate double bond and not in excess of 12 carbon atoms.

5. Method according to claim 1 in which said hydrocarbons are olefins having a terminal double bond.

6. Method according to claim 1 in which said hydrocarbons are branched chain unsaturated hydrocarbons.

7. Method according to claim 1 in which said unsaturated hydrocarbons contain admixed therewith aromatic hydrocarbons.

8. Method according to claim 1 in which R is a monovalent saturated aliphatic hydrocarbon radical having the same number of carbon atoms as at least one of the unsaturated hydrocarbons.

9. Method according to claim 1 in which said unsaturated hydrocarbons contain admixed therewith materials substantially inert to said activators.

10. Method according to claim 9 in which said inert materials are substantially saturated aliphatic hydrocarbons.

11. Method for dimerizing α-olefins having at least 3 carbon atoms, which comprises heating such olefins at a temperature of about 160–220° C. in the presence of a dimerization activator having the general formula Me(R)ₙ in which Me is a metal selected from the group consisting of beryllium, aluminum, gallium and
indium, R is at least one substituent selected from the group consisting of hydrogen, monovalent saturated aliphatic hydrocarbon radicals and monovalent aromatic hydrocarbon radicals, and n is the valence of the metal Me, and recovering a dimer.

12. Method according to claim 11 in which said heating is effected at increased pressure.

13. Method according to claim 11 in which said olefin is propylene and said recovered dimer is 1-methyl-1-propyl-ethylene.

14. Method for dimerizing olefins having a double bond in the intermediate position which comprises heating such olefins at a temperature of about 120 to 250° C. in the presence of dimerization activator having the general formula Me(R)\(_n\), in which Me is one metal selected from the group consisting of beryllium, aluminum, gallium and indium, R is at least one substituent selected from the group consisting of hydrogen, monovalent saturated aliphatic hydrocarbon radicals and monovalent aromatic hydrocarbon radicals, and n is the valence of the metal Me, and recovering a dimer.

References Cited in the file of this patent

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,117,022</td>
<td>Cramer</td>
<td>May 10, 1938</td>
</tr>
<tr>
<td>2,270,292</td>
<td>Grosse</td>
<td>Jan. 20, 1942</td>
</tr>
<tr>
<td>2,401,922</td>
<td>Frey et al.</td>
<td>June 11, 1946</td>
</tr>
<tr>
<td>2,440,498</td>
<td>Young et al.</td>
<td>Apr. 27, 1948</td>
</tr>
</tbody>
</table>

OTHER REFERENCES