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CONVERSION OF ALIPHATIC HYDROCARBONS TO AROMATIC HYDROCARBONS

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This invention relates to the conversion of aliphatic hydrocarbons containing at least six carbon atoms and containing a quaternary carbon atom, and more particularly to the conversion of such hydrocarbons to aromatic hydrocarbons.

Various methods have been proposed and utilized for the dehydrogenation of organic compounds. Thus, ethylene is made by the dehydrogenation of ethane; butylenes-1 and -2 by the dehydrogenation of n-butane; isobutylene by the dehydrogenation of isobutane; butadiene by the dehydrogenation of n-butane, and/or of the n-butenes; benzene by the dehydrogenation of cyclohexane; toluene by the dehydrogenation of methylcyclohexane; the xylenes by the dehydrogenation of the dimethylcyclohexanes, and the like. Also, it is known to dehydroisomerize certain compounds, such as in the conversion of methylcyclopentane to benzene and of dimethylcyclopentane to toluene. These prior processes are usually high temperature pyrolysis operations or are heterogeneous phase catalytic operations.

It is a principal object of the present invention to provide an improved process for the conversion of a particular class of hydrocarbons. More specifically, a particular object of the invention is to provide a process for the dehydroisomerization of aliphatic hydrocarbons containing at least six carbon atoms and containing a quaternary carbon atom, to a product which contains at least one less quaternary carbon atom. A more specific object is to provide a process for the dehydroisomerization and cyclization of 2,4,4-trimethylpentene to an aromatic hydrocarbon. Another specific object is to provide a process for the dehydroisomerization and cyclization of 2,2,5-trimethylhexane to an aromatic hydrocarbon. These objects will be more fully understood and others will become apparent from the description of the invention.

Now, in accordance with the present invention, it has been found that an aliphatic hydrocarbon which contains at least six carbon atoms and contains a quaternary carbon atom is converted, in the presence of a substantial proportion of free iodine, at an elevated temperature to a hydrocarbon which contains at least one less quaternary carbon atom. Furthermore, when there is only one quaternary carbon atom in a chain of at least five contiguous carbon atoms (at least four in addition to the quaternary carbon atom), the hydrocarbon reacts with iodine at an elevated temperature to undergo isomerization and further may also be cyclized to a cyclic hydrocarbon, and particularly dehydrocyclized to an aromatic hydrocarbon. The at least four carbon atoms may be distributed to provide only two carbon atoms on either side of the quaternary carbon atom or so as to provide a chain of at least three contiguous carbon atoms on one side.

The invention is applicable particularly to aliphatic hydrocarbons which contain only one quaternary carbon atom in a chain of at least five contiguous carbon atoms and the quaternary carbon atom is joined to a chain of from three to five contiguous carbon atoms, as illustrated by 2,2,4-trimethylpentane, 2,4,4-trimethylpentene-1, 2,2,3-trimethylpentane, 2,2,4-trimethylhexane, 3,3,4-trimethylhexane, 2,2,5-trimethylhexane and 2,4,4-trimethylhexane.

When the hydrocarbon contains two quaternary carbon atoms in a chain of at least four carbon atoms the reaction involves a dehydroisomerization coupled with a further dehydroisomerization and/or dealkylation leading by cyclization to the formation of a chain of six non-quaternary carbon atoms in an aromatic ring.

The reaction of the hydrocarbon and the iodine is suitably carried out by heating a mixture of them to a temperature sufficiently elevated to effect a dehydrogenation reaction of the iodine with the hydrocarbon. The reaction is carried out in vapor phase and can be effected by passing the mixture of reactants through a suitable heated reaction zone, which may be unobstructed, or it can be suitably provided with particulate solid material to increase the heat transfer rate, intermingling of the reacant molecules, and the like. Such solid material will usually be chemically inert toward the reactants under the conditions of the process, although it will be understood that materials can be utilized which exert some desirable catalytic effect upon the reactants or on the products, provided the essential reaction of the invention is not materially interfered with. The reaction is readily effected by suitably heating the hydrocarbon and iodine vapors under atmospheric pressure. However, pressures either lower than or higher than atmospheric pressure can be utilized.

Diluent vapors of other substances can be admixed with the reactants in order to reduce the concentrations thereof at a given temperature and under a given total pressure. Other dehydrogenating agents, particularly such as oxygen, sulfur and the like, can be incorporated in the reactant mixture provided they do not materially change the nature of the hydrocarbon product. Thus, oxygen can be added, either at a single point in the flow, either ahead of, or in the reaction zone, or at a plurality of points in the reaction zone. Such an oxidizing agent, of course, will react with the hydrogen iodide to form water and liberate free iodine.

In general, the reaction can be carried out at temperatures within a broad range of temperatures. Thus, temperatures ranging from 300° C. to 600° C. are suitable, even though still lower and still higher temperatures are useful, particularly depending on the particular hydrocarbon reactant and the particular product desired. Particularly useful temperatures range from about 350° C. to about 550° C. It will be understood, of course, that in the case of a given reactant more severe temperature conditions can be utilized while at the same time utilizing a short residence time in the reaction zone.

The residence time of the hydrocarbons under the reaction conditions is in general relatively small, ranging from a fraction of a second, e.g., 0.01 second, up to as high as several minutes, e.g., 3–5, with from about 0.1 to 60 seconds being satisfactory in the usual cases. This, as already indicated, depends in part on the temperature of the reaction zone. Other factors which are determinative of the residence time of the hydrocarbon include the molar ratio of iodine to hydrocarbon, the nature of the desired product, and the particular hydrocarbon reactant utilized.

Since the dehydrogenation involves the reaction of free iodine with the hydrogen to be removed from the hydrocarbon, the proportion of iodine used in the reaction depends on the extent of the dehydrogenation of the individual molecules, whether to form a mono-olefin from a saturated hydrocarbon, a diolefin from a saturated

hydrocarbon, a diolefin from a mono-olefinic hydrocarbon, an aromatic hydrocarbon from a saturated aliphatic hydrocarbon, or an aromatic hydrocarbon from an unsaturated aliphatic hydrocarbon, etc., as well as the percentage conversion of the hydrocarbon which is desired in a single passage through the reaction zone. In general, from about 0.05 to about 3 or 4 equivalents of iodine can be utilized for each equivalent of hydrogen to be removed to yield the desired hydrocarbon product, although it is usually preferable to utilize at least about 0.2 equivalent and amounts corresponding to no more than about one equivalent give satisfactory results.

Although the nature of the isomerization reaction which occurs is not entirely understood, the evidence indicates that there is a cleavage of the bond joining the quaternary carbon atom to one of the carbon atoms and the formation of a new C-to-C linkage between the carbon atom from which the quaternary carbon atom is cleaved and one of the other carbon atoms bonded directly to the quaternary carbon atom. The presence of a chain of at least two, and particularly three, non-quaternary carbon atoms attached to the quaternary carbon atom appears to be particularly favorable to the isomerization. For example, the results from the reaction of 2,2,4-trimethylpentane suggest that during the course of the reaction the 2,2,4-trimethyl-C_5-hydrocarbon-chain structure is isomerized to a 2,5-dimethyl-C_6-hydrocarbon structure; similarly, in the case of 2,4,4-trimethylpentene-1. In the case of 2,2-dimethylpentane, the isomerization gives a 2-methyl-C_6-hydrocarbon structure. Similarly, isomerization of 3,3-dimethylpentane yields a 3-methyl-C_6-hydrocarbon structure. Dehydroaromatization of this structure gives toluene. As stated hereinbefore, those hydrocarbons which give rise by isomerization to a chain of six non-quaternary carbon atoms are recoverable at least to a substantial extent in the form of the cyclized and dehydrogenated six-carbon ring hydrocarbons, namely, aromatic hydrocarbons.

Having described the general features of the invention and various factors which are involved in its practice, details thereof will be illustrated by the following illustrative examples, which are not to be considered as limiting thereon.

Example I

A vaporous mixture of iodine of 2,2,4-trimethylpentane in a molar ratio of iodine/hydrocarbon of 0.31 was passed through an empty Vycor reactor (4 cm. inside diameter; 811 cc. volume) at a temperature of 444° C. and one atmosphere pressure at a nominal residence time, based on total molar input at reaction temperature, of 26 seconds. The product stream was collected and analyzed to determine the nature and proportions of the components thereof. Based on the analysis, 34% of the hydrocarbon feed was reacted. The reacted iodine occurred in the product stream essentially as hydrogen iodide, with a very small proportion in the form of C_1 to C_4 iodides, while the hydrogen was accounted for essentially entirely as hydrocarbon or hydrogen iodide. For each 100 moles of hydrocarbon reacted, 30.1 were accounted for as C_8-hydrocarbons (21.8 as C_8 olefin, principally 2,4,4-trimethylpentene, 7.8 as p-xylene, 0.4 as m-xylene and 0.07 as o-xylene) and 68.5 moles were accounted for as C_4-hydrocarbons, isobutane and isobutene.

Since the formed 2,4,4-trimethylpentene is a precursor for aromatics, as seen from Example III, it is clear that in this example the limited proportion of free iodine used was limiting on the yield of aromatics. Although cleavage to two iso-C_4 fragments was the principal result from the reaction under the conditions of Example I, the iso-C_4 products are readily convertible again to the 2,2,4-trimethyl-C_5 structure, so that their formation does not represent any net loss.

Example II

A vaporous mixture of iodine and 2,2,5-trimethylhexane in a molar ratio of iodine/hydrocarbon of 1.0 was passed through the reactor of Example I at a temperature of about 475° C. (462–488° C., inlet and outlet, respectively) and one atmosphere pressure at a nominal residence time of 8 seconds. Based on analysis of the product stream from the reactor, 69% of the hydrocarbon reacted and ≧80% of the iodine reacted. The iodine was essentially entirely present as hydrogen iodide and free iodine, and the reaction was clean with the essential absence of coke formation. For each 100 moles of the hydrocarbon reacted, the product contained about 67 moles of C_9-monoalkene and of the order of 3 moles of C_9-alkadiene (there was practically no cycloalkane or cycloalkene), a portion of aromatic hydrocarbon, all being C_8 or lower, there being 4.2 moles of m-xylene, about 15 moles of iso-C_5-hydrocarbons and about 17 moles of iso-C_4-hydrocarbons, being essentially isopentane, isopentene, isobutane and isobutene.

Example III

A vaporous mixture of iodine and diisobutylene (21% 2,4,4-trimethylpentene-2 and 79% 2,4,4-trimethylpentene-1) in a molar ratio of iodine/hydrocarbon of 0.3 was passed through the reactor of Example I at a temperature of about 440° C. (425–454° C., inlet and outlet, respectively) and one atmosphere pressure at a nominal residence time of 10 seconds. Based on analysis of the product stream from the reactor, 32% of the hydrocarbon and ≧75% of the iodine reacted. The iodine was present as hydrogen iodide and free iodine, together with a small amount of C_8 and C_4 iodides, and the reaction was clean with the essential absence of coke formation. On the basis of 100 moles of the hydrocarbon reacted, the product stream contained: 28 moles of C_8H_{18} (principally 2,2,4-trimethylpentane), 9 moles of C_8 diolefin, 35 moles of paraxylene, 16 moles of isobutane, 28 moles of isobutylene, 1 mole of methane, and 0.5 mole of hydrogen.

The isobutane is convertible to isobutene, which, together with that formed in the reaction, is convertible to diisobutylene. This, together with the non-aromatic C_8-hydrocarbons recoverable from the reaction product stream is suitably recycled with iodine to the reaction zone for the production of further amounts of aromatic (p-xylene).

We claim as our invention:

1. A process for the conversion of an aliphatic hydrocarbon which contains a chain of at least four carbon atoms and in which the sum of (1) the total number of carbon atoms in the chain plus (2) the number of quaternary carbon atoms in the chain is at least six and the longest chain contains no more than five contiguous non-quaternary carbon atoms into an aromatic hydrocarbon containing no quaternary carbon atom, which comprises subjecting a mixture of said hydrocarbon and at least about 0.3 mole of iodine per mole of hydrocarbon in vapor phase for a time of from 0.01 second to five minutes to a temperature of at least 300° C. to effect a bond cleavage in the hydrocarbon in the presence of free iodine and convert a quaternary carbon atom of the hydrocarbon to a non-quaternary carbon atom, and recovering an aromatic hydrocarbon product.

2. A process in accordance with claim 1, wherein the hydrocarbon is an alkane.

3. A process in accordance with claim 1, wherein the hydrocarbon is an alkene.

4. A process in accordance with claim 1, wherein the quaternary carbon atom of the hydrocarbon is in a chain of only five contiguous carbon atoms.

5. A process in accordance with claim 1, wherein the quaternary carbon atom of the hydrocarbon is in a chain of only six contiguous carbon atoms.

6. A process in accordance with claim 4, wherein the hydrocarbon is 2,2,4-trimethylpentane.

7. A process in accordance with claim 4, wherein the hydrocarbon is 2,4,4-trimethylpentene-1.

8. A process in accordance with claim 5, wherein the hydrocarbon is 2,2,5-trimethylhexane.

References Cited in the file of this patent

UNITED STATES PATENTS

1,925,421 Van Peski ---------- Sept. 5, 1933

2,315,499 Cantzler et al. ---------- Apr. 6, 1943
2,492,844 Condon ---------- Dec. 27, 1949

OTHER REFERENCES

Chemical Abstracts, vol. 25 (1931), page 5967[9].

Bairstow et al.: "Journal of the Chemical Society" (1933), p. 1158.

Rossini et al.: "Hydrocarbon from Petroleum" (1953), page 406, Reinhold Publishing Corp., New York.