

UNITED STATES PATENT OFFICE

2,291,254

CONVERSION OF HYDROCARBONS

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No Drawing. Application July 14, 1941,
Serial No. 402,436

7 Claims. (Cl. 260-666)

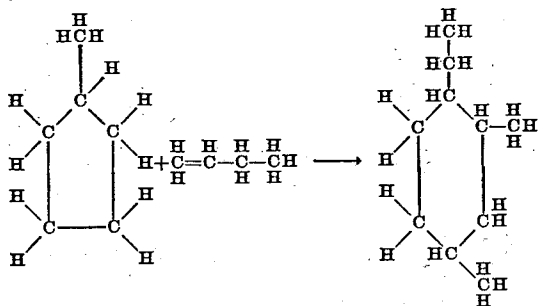
This invention relates to a process for hydrocarbon conversion and more particularly to a process for converting alkyl cyclopentanes to alkyl cyclohexanes by reacting the alkyl cyclopentanes with olefins in the presence of a catalyst.

The present process is a contribution to the art of producing reactions between different types of hydrocarbons to synthesize other hydrocarbon compounds of increased molecular weight. It is known that various alkylated naphthenic hydrocarbons can be formed hypothetically by adding alkyl radicals to the base members of the respective series, such as, for example, cyclopentane, cyclohexane, etc. The building up of the various homologs does not follow such a simple mechanism, however, the reactions actually involve shifting of labile hydrogen atoms and readjustment of valences. The naphthenes as a group may include cycloparaffins or any hydrocarbon containing a saturated ring structure in the molecule.

It is recognized that the alkylation of naphthenes in general is not new. The present process is particularly concerned with a simultaneous isomerization and alkylation of alkyl cyclopentanes with olefins to produce alkyl cyclohexanes. Alkyl cyclopentanes are found to occur naturally in substantial quantities in certain petroleum fractions and in most cases are more reactive than the corresponding cyclohexane compounds.

In one specific embodiment the present invention comprises a process for the reaction of alkyl cyclopentane hydrocarbons with olefins in the presence of a sulfuric acid catalyst at relatively low temperatures in the range of about -40 to about $+120^{\circ}\text{C}$.

The general type of reaction which is effected by the present process is typified by the following equation showing the formation of 1-ethyl-2,4-dimethyl cyclohexane from methyl cyclopentane and normal butylene.



The ease with which the above reaction occurs is probably due to the presence of a tertiary carbon atom in the methyl cyclopentane molecule. Owing to the difficulty of following the character

of such reactions and the invariable formation of certain proportions of intermediate addition compounds with the organic radical in the catalyst in reactions of the present character, the above explanation is not offered as entirely adequate. It also omits mention of the formation of more highly alkylated compounds and the formation of olefin polymers which is unavoidable to some extent in these reactions. However, under properly controlled conditions, which will be presently specified, the polymerization reactions may be kept at a minimum and the alkylation-isomerization reactions may be regulated by controlling the temperature, the amount of catalyst, and the proportion of olefins to alkyl cyclopentane hydrocarbons, so that the maximum yields of the desired compounds will be produced.

It has been discovered that the isomerization of alkyl cyclopentanes to alkyl cyclohexanes can be accomplished more advantageously by the present invention than by straight isomerization alone. In this process the alkyl cyclopentanes are reacted with olefins in the presence of a sulfuric acid catalyst. We have found that under the preferred conditions of the process the product of the alkylation reaction consists not of a cyclopentane derivative but of a cyclohexane derivative. In other words, isomerization occurs simultaneously with the alkylation reaction, although the sulfuric acid is not ordinarily an isomerizing catalyst for alkyl cyclopentanes and will not cause the isomerization of alkyl cyclopentanes in the absence of other hydrocarbons. By this reaction the isomerization of alkyl cyclopentanes to alkyl cyclohexanes is accomplished at a much lower temperature and more rapidly. Since this simultaneous isomerization-alkylation reaction occurs at somewhat lower temperatures than the straight isomerization reaction, undesirable side reactions are minimized and the reaction is more easily controlled. Another advantage lies in the fact that nearly complete conversion of the alkyl cyclopentanes can be obtained. The cyclohexane derivatives produced by this process may be dehydrogenated readily to produce valuable alkyl aromatics.

The olefins employed in the process may include normally gaseous olefins and/or liquid olefins such as pentenes, olefin polymers, and cycloolefins although they are not necessarily equivalent in action. The normal butylenes are particularly advantageous in that they give a high proportion of the desired reaction with a minimum of undesirable side reactions. It is not necessary, however, to use a pure olefin as any olefin-containing hydrocarbon fraction may be employed, for instance, a gas from a cracking process which is rich in butylenes can be used.

The details of operation of the present process are comparatively simple. The cyclopentane de-

rivatives involved in the reactions are liquid at ordinary temperatures, and the process may be conducted merely by passing the gaseous olefins such as normal butylenes or mixtures of olefins into an emulsion of sulfuric acid and an alkyl cyclopentane until the desired reaction is effected. Such reactions may be accelerated by the use of superatmospheric pressures which increase the effective concentration of the olefin employed. Usually it is desirable to maintain a higher concentration of the alkyl cyclopentane than olefins in the reaction zone.

It is characteristic of the present process that when operating at ordinary temperatures the isomerization-alkylation reactions predominate over the polymerization reaction among the olefins used, even at pressures above atmospheric. The pressure at which the reaction should be carried out will depend on the temperature. At temperatures below the boiling point of the olefins, atmospheric pressures can be used. When the temperatures are higher superatmospheric pressures are preferable. The temperature of the reaction may vary greatly depending upon the amount and concentration of the catalyst and upon the concentrations of the reactants. In general, the temperatures used may be between about -40 and $+120^{\circ}\text{C}$. It is advisable, however, to keep the reaction at relatively low temperatures since at higher temperatures the rate of the undesirable reactions increases rapidly. The preferred reaction temperature is between about 0 and $+50^{\circ}\text{C}$.

The ratio of acid catalyst to hydrocarbon in the reaction zone will depend on the temperature, pressure, type of hydrocarbon, etc. In general, the ratio of acid to hydrocarbon in the reaction zone will be in the range of from about 1:1 to about 1:4. The molal ratio of alkyl cyclopentane hydrocarbons to olefins used will vary. It is preferred, however, to have an excess of alkyl cyclopentane hydrocarbons in the reaction zone. A suitable proportion of olefin in the total hydrocarbon present in the reaction zone may be in the range of 25 to 50%. Pure alkyl cyclopentane hydrocarbons may be used as charge or hydrocarbon mixtures containing a substantial proportion of alkyl cyclopentanes such as some straightrun gasoline or other gasoline fractions. Instead of a pure olefin, cracked gases rich in the desired olefins may be employed.

In one method of operating this process the liquid alkyl cyclopentanes are placed in a reaction vessel with the sulfuric acid catalyst. The olefin is introduced below the surface of the liquid in the reaction vessel which is maintained in a state of emulsion by a stirring device. The olefin gases bubble through the emulsion of hydrocarbon and catalyst and are reacted with the methyl cyclopentane. Upon completion of the reaction the sulfuric acid and hydrocarbon phases are separated and the upper hydrocarbon layer is decanted and subjected to distillation. The process is not limited to batch operations but may be made continuous by the adoption of necessary modifications in conformity with other commercial operations.

The sulfuric acid used as catalyst for the reaction is preferably of a concentration between 85 and 100%, and even 5 to 10% of sulfuric anhy-

dride may be present in the 100% sulfuric acid. This sulfuric acid catalyst is suitable without further modification but may also be modified by the addition of spacing agents such as soluble metal salts or salts of organic acids and bases. These modifying or spacing agents in some cases further reduce the amounts of undesirable reactions such as polymerization, etc.

The following example is given as typical of the results obtainable when practicing the present process. However, the data presented should not be construed as imposing undue limitations upon its scope.

Normal butylenes were bubbled for $2\frac{1}{2}$ hours through a reaction mixture consisting of 3 mols of methyl cyclopentane and 2.75 mols of sulfuric acid contained in a flask maintained at 16°C . The normal butylenes introduced amounted to 2.25 mols. The liquid hydrocarbon product when analyzed contained 45% unreacted methyl cyclopentane, 33% alkylated cyclohexane, and 22% of other hydrocarbons.

The foregoing specification is illustrative of the operation of the process of the present invention and the example cited shows the advantages to be gained by its utilization and practice. Neither the specification nor the example are to be construed as imposing undue limitations upon its generally broad scope.

We claim as our invention:

1. A process for producing substantial yields of alkyl substituted cyclohexanes from alkyl cyclopentanes which comprises reacting an alkyl cyclopentane with an olefin hydrocarbon in the presence of a sulfuric acid catalyst.

2. A process for producing substantial yields of alkyl substituted cyclohexanes from alkyl cyclopentanes which comprises reacting an alkyl cyclopentane with an olefin hydrocarbon in the presence of a sulfuric acid catalyst at a temperature between about -40 and about $+120^{\circ}\text{C}$.

3. A process for producing substantial yields of alkyl substituted cyclohexanes from alkyl cyclopentanes which comprises reacting an alkyl cyclopentane with an olefin hydrocarbon in the presence of a sulfuric acid catalyst at a temperature between about 0 and about $+50^{\circ}\text{C}$.

4. A process for producing substantial yields of alkyl substituted cyclohexanes from alkyl cyclopentanes which comprises reacting an alkyl cyclopentane with normal butylene in the presence of a sulfuric acid catalyst.

5. A process for producing 1-ethyl-2,4-dimethyl cyclohexane which comprises reacting methyl cyclopentane with normal butylenes in the presence of a sulfuric acid catalyst.

6. A process for producing 1-ethyl-2,4-dimethyl cyclohexane which comprises reacting methyl cyclopentane with normal butylene in the presence of a sulfuric acid catalyst at a temperature of between about 0 and about $+50^{\circ}\text{C}$.

7. A process for treating a gasoline boiling range hydrocarbon fraction containing alkyl cyclopentanes to produce alkyl cyclohexanes from said alkyl cyclopentanes which comprises treating said gasoline boiling range hydrocarbon fraction with olefin-containing gases in the presence of a sulfuric acid catalyst.

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