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CONVERSION OF HYDROCARBONS

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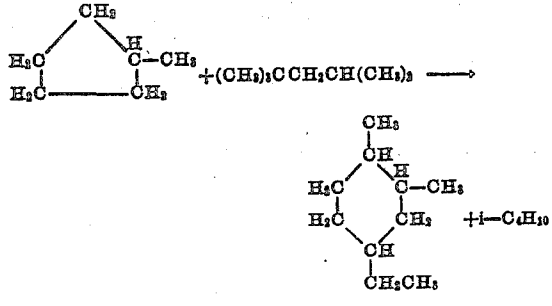
7 Claims. (Cl. 260—666)

This invention relates to a process for effecting hydrocarbon conversions and more particularly to a process for converting alkyl cyclopentane hydrocarbons into alkyl cyclohexanes by reacting said alkyl cyclopentane hydrocarbons with paraffinic hydrocarbons 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 increasing molecular weight. Various alkylated cyclopentane hydrocarbons can be illustrated by adding alkyl radicals to the base member of this series, namely cyclopentane. However, the actual syntheses of different alkyl cyclopentane and alkyl cyclohexane hydrocarbons do not follow such a simple mechanism.

One specific embodiment of the present invention comprises a process for reacting an alkyl cyclopentane hydrocarbon with a paraffinic hydrocarbon in the presence of an alkylating catalyst to form a substantial yield of alkylated and polyalkylated cyclohexane hydrocarbons.

The present process is particularly concerned with a simultaneous cleavage or breaking of a paraffinic hydrocarbon and the alkylation of an alkyl cyclopentane with fragments resulting from said cleavage or breaking of a paraffinic hydrocarbon. Furthermore, it appears that isomerization can accompany alkylation when an alkyl cyclopentane hydrocarbon is destructively alkylated with a paraffinic hydrocarbon. The following equation illustrates the destructive alkylation of methyl cyclopentane with iso-octane:



The above equation indicates that methyl cyclopentane may be reacted with 2,2,4-trimethylpentane to form 1,2-dimethyl-4-ethyl cyclohexane together with isobutane. Other branched chain paraffinic hydrocarbons and less-branched chain paraffinic hydrocarbons can also undergo a similar reaction under suitable conditions of operation to form alkylated cyclohexane hydrocarbons and paraffinic hydrocarbons of lower molecular weight than those charged to the process.

The ease with which the above reaction occurs is probably due to the presence of a tertiary carbon atom in the alkyl cyclopentane molecule. Because of the difficulty in following the character of such reactions and the possible formation of certain proportions of intermediate addition compounds with the catalyst in reactions of the present type, the above explanation is not offered as being entirely adequate. It also omits mention of the formation of small amounts of gaseous hydrocarbons of low molecular weight such as methane and ethane which sometimes occurs to a minor extent. However, under properly controlled conditions, decomposition reactions to undesired gaseous hydrocarbons may be kept low and the alkylation may be regulated by controlling the temperature, the nature and amount of the catalyst, the proportion of paraffinic hydrocarbons to alkyl cyclopentane hydrocarbons, etc., so that high yields of the desired compounds will be produced.

We have discovered that isomerization and alkylation of alkyl cyclopentane hydrocarbons can be accomplished simultaneously and more advantageously by the process of the present invention than by isomerization alone. In this process, the alkyl cyclopentanes are reacted with straight and/or branched chain paraffins in the presence of an alkylating catalyst including sulfuric acid, hydrogen fluoride, mixtures of hydrogen fluoride and boron fluoride, and Friedel-Crafts type metal halides together with a hydrogen halide. Under the preferred conditions of operation, which are discussed hereinafter in relation to the different alkylating catalysts, an alkylation product is formed consisting not of more highly alkylated cyclopentane hydrocarbons but of alkylated cyclohexane hydrocarbons. In other words, isomerization occurred either before, after, or during the alkylation reaction. By this process, the alkylation of alkyl cyclopentane hydrocarbons with paraffinic hydrocarbons, including isoparaffins and normal paraffins, to form alkyl cyclohexane hydrocarbons is accomplished rapidly under operating conditions which are relatively easy to control.

Another advantage of the process is the fact that nearly complete conversion of the alkyl cyclopentane hydrocarbons into alkyl cyclohexanes can be obtained. Furthermore, the cyclohexane hydrocarbons formed by this process may be separated from unconverted cyclopentane hy-

drocarbons and dehydrogenated catalytically or thermally into alkyl benzene hydrocarbons while the unconverted or incompletely converted alkyl cyclopentane hydrocarbons are returned to further treatment with paraffinic hydrocarbons in the presence of an alkylating catalyst as herein set forth.

The different alkyl cyclopentane hydrocarbons and paraffinic hydrocarbons employed in the process need not be entirely pure as any hydrocarbon fraction or fractions containing alkyl cyclopentane hydrocarbons and paraffinic hydrocarbons may be utilized in the process. Thus, a hydrocarbon fraction containing substantial amounts of methyl-, ethyl-, and higher alkyl cyclopentanes in admixture with straight and branched chain paraffins may be converted as herein set forth to obtain substantial yields of alkyl cyclohexane hydrocarbons.

The catalysts employed in the process of the present invention are not necessarily equivalent in their action and accordingly, the conditions of operation and particularly the reaction temperature are dependent upon the catalyst employed in a particular reaction. Thus, with hydrogen fluoride or mixtures of hydrogen fluoride and boron fluoride, a reactor temperature of from about −20° to about 200° C. is employed at a pressure of generally not more than about 35 atmospheres; while sulfuric acid is utilizable generally at a temperature of from about −5° to about 120° C. When employing catalysts containing an acid of phosphorus, such as solid phosphoric acid, the temperature utilized is from about 100° to about 450° C. and the pressure is generally between about 1 and 70 atmospheres. Catalysts of the Friedel-Crafts type are utilizable under different conditions of operation depending upon the particular Friedel-Crafts type catalyst employed. Thus, aluminum chloride may be utilized at a temperature of from about −70° to about 150° C. while ferric chloride requires a somewhat higher average temperature and zinc chloride is utilizable only at still higher temperatures and particularly at a temperature of from about 150° to about 450° C.

The details of operation of the present process are relatively simple since alkyl cyclopentane hydrocarbons are liquid under ordinary conditions of temperature and pressure. Accordingly, the process of the present invention is carried out by contacting an alkyl cyclopentane hydrocarbon with a paraffinic hydrocarbon generally containing 4 or more carbon atoms per molecule in the presence of an alkylating catalyst under the preferred operating conditions until alkylation has occurred and a substantial yield of an essentially saturated hydrocarbon product is formed containing a relatively high proportion of alkyl cyclohexane hydrocarbons. The molar ratio of alkyl cyclopentane hydrocarbons to paraffinic hydrocarbons should be greater than 1 and preferably greater than 3, the exact ratio being somewhat dependent upon the particular alkyl cyclopentane and paraffinic hydrocarbons charged to the process. The ratio of alkyl cyclopentane hydrocarbon to paraffinic hydrocarbons charged is subject to some variation and is affected considerably by the method of introducing the paraffinic hydrocarbon, the efficiency of mixing, etc.

It is advisable to carry out the process of the present invention at as low a temperature as possible and as is practical, since at higher temperatures there is generally a marked increase in the rate of undesirable reactions which frequently result in deposition and/or degradation of the desired alkylation product.

While the process of the present invention may be effected in either batch or continuous types of operation, it is usually carried out on a continuous basis by withdrawing from the reaction zone a complex mixture of excess unreacted alkyl cyclopentanes, desired alkylated cyclohexanes, higher boiling hydrocarbons, and catalyst; said complex mixture being withdrawn at substantially the same rate as that at which the hydcarbons charged are supplied to the alkylation reactor. At least a portion of the recovered used catalyst and unreacted alkyl cyclopentanes may be recycled to further treatment with paraffinic hydrocarbons in the presence of some freshly added alkylating catalyst.

Batch type operation of the present process may be carried out by gradually introducing a paraffinic hydrocarbon fraction or a paraffin containing fraction to a reaction vessel containing a mixture of the alkyl cyclopentane hydrocarbon and the catalyst. The reaction vessel is preferably equipped with an efficient mixing or stirring device so as to insure intimate contact of the reacting hydrocarbons and catalyst. Upon completion of the alkylation reaction, a hydrocarbon product is separated from the catalyst and said hydrocarbon product is further fractionally distilled to separate alkylated cyclohexane hydrocarbons from unconverted or incompletely converted paraffinic and cycloparaffinic hydrocarbons which are returned to further treatment in the presence of an alkylating catalyst as hereinabove set forth.

The following example indicates results obtainable by the present process, although it is introduced with no intention of limiting the scope of the invention in exact correspondence thereto.

4 molecular proportions of methyl cyclopentane are reacted with 0.5 molecular proportions of 2,2,4-trimethyl pentane in the presence of hydrogen fluoride at a temperature of 100° C. The resultant reaction mixture, after separation therefrom of unconverted methyl cyclopentane and 2,2,4-trimethyl pentane, contains substantial amounts of alkylated cyclohexane hydrocarbons.

The character of the present invention and its novelty and utility in producing alkyl cyclohexane hydrocarbons can be seen from the preceding specification and example, although neither section is intended to limit unduly its generally broad scope.

We claim as our invention:

1. A process for producing substantial yields of alkyl cyclohexane hydrocarbons which comprises reacting an alkyl cyclopentane hydrocarbon and an isoparaffinic hydrocarbon in the presence of an alkylating catalyst while maintaining a molar excess of alkyl cyclopentane hydrocarbon to isoparaffinic hydrocarbon throughout the reaction.

2. A process for producing substantial yields of alkyl cyclohexane hydrocarbons which comprises reacting an alkyl cyclopentane hydrocarbon and an isoparaffinic hydrocarbon in the presence of an alkylating catalyst comprising sulfuric acid as its essential active ingredient.

3. A process for producing substantial yields of alkyl cyclohexane hydrocarbons which comprises reacting an alkyl cyclopentane hydrocarbon and an isoparaffinic hydrocarbon in the presence of an aykylating catalyst comprising hydrogen fluoride as its essential active ingredient.

4. A process for producing substantial yields of alkyl cyclohexane hydrocarbons which comprises reacting an alkyl cyclopentane hydrocarbon and an isoparaffinic hydrocarbon in the presence of an alkylating catalyst comprising a Friedel-Crafts type metal halide as its essential active ingredient.

5. A process for producing substantial yields of alkyl cyclohexane hydrocarbons which comprises reacting an alkyl cyclopentane hydrocarbon and a paraffinic hydrocarbon in the presence of an alkylating catalyst while maintaining a molar excess of alkyl cyclopentane hydrocarbon to paraffinic hydrocarbon throughout the entire reaction.

6. A process for producing substantial yields of alkyl cyclohexane hydrocarbons which comprises reacting an alkyl cyclopentane hydrocarbon and an isoparaffinic hydrocarbon in the presence of an alkylating catalyst while maintaining a molar ratio of alkyl cyclopentane hydrocarbon to isoparaffinic hydrocarbon of more than three throughout the reaction.

7. A process for producing substantial yields of alkyl cyclohexane hydrocarbons which comprises reacting an alkyl cyclopentane hydrocarbon and a paraffinic hydrocarbon in the presence of an alkylating catalyst while maintaining a molar ratio of alkyl cyclopentane hydrocarbon to paraffinic hydrocarbon of more than three throughout the reaction.

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