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CONVERSION OF HYDROCARBONS

Herman Pines and Vladimir N. Ipatieff, Chicago, Ill., assignors to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

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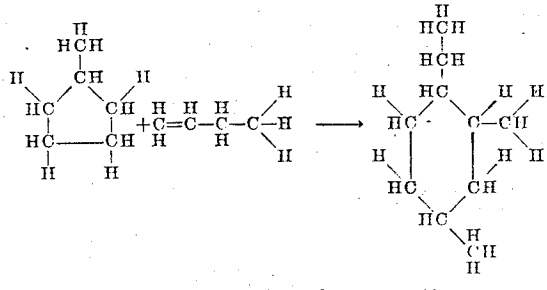
This invention relates to a process for hydrocarbon conversion and more particularly to a process for converting alkyl cyclopentanes to alkyl cyclohexanes by reacting the alkyl cyclopentanes with olefins in the presence of a catalyst.

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, as the reactions apparently involve a shifting of labile hydrogen atoms and a readjustment of valences. The naphthenes as a group may include cycloparaffins or any hydrocarbon containing a saturated ring structure in the molecule.

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 reacting alkyl cyclopentane hydrocarbons with olefinic hydrocarbons in the presence of a hydrogen fluoride catalyst.

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 a normal butene.



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, polymerization reactions may be kept low and the alkylation-isomerization may be regulated by controlling the temperature, the amount of catalyst, and the proportion of olefins to alkyl cyclopentane hydrocarbons, so that high yields of the desired compounds will be produced.

We have discovered that the isomerization of alkyl cyclopentanes to alkyl cyclohexanes can be accomplished more advantageously by the process of the present invention than by isomerization alone. In this process the alkyl cyclopentanes are reacted in the presence of hydrogen fluoride with olefins containing preferably at least 3 carbon atoms per molecule. Under the preferred conditions of the process as hereinafter set forth, a product of the alkylation reaction is formed consisting not of cyclopentane hydrocarbons but of cyclohexane hydrocarbons. In other words, isomerization occurs simultaneously with the alkylation reaction, although hydrogen fluoride is not ordinarily an isomerizing catalyst for alkyl cyclopentanes and does not cause the isomerization of alkyl cyclopentanes in the absence of other hydrocarbons such as olefins. By this reaction the isomerization of alkyl cyclopentanes to alkyl cyclohexanes is accomplished rapidly and at a relatively low temperature. Since the simultaneous isomerization and alkylation reactions occur at somewhat lower temperatures than the straight isomerization reaction, undesirable side reactions are kept low and the process is relatively easy to control.

Another advantage of the process resides in the fact that nearly complete conversion of the alkyl cyclopentanes into the alkyl cyclohexanes can be obtained. The cyclohexane hydrocarbons so produced by this process may be separated from unconverted cyclopentanes and dehydrogenated catalytically or thermally to alkyl aromatic hydrocarbons while the unconverted or incompletely converted alkyl cyclopentane hydrocarbons are returned to further treatment with olefins in the presence of the hydrogen fluoride catalyst. Aromatic hydrocarbons other than the desired alkyl

aromatics formed by such dehydrogenation may be recycled to the alkylating zone to which the fresh alkyl cyclopentanes and olefinic hydrocarbons are charged.

The olefins which may be employed in the process are both normally gaseous and normally liquid olefins and preferably comprise those containing at least 3 carbon atoms per molecule. Cycloolefins and polymers of normally gaseous olefins are also utilizable as alkylating agents although they are not necessarily equivalent in their action. The normal butenes are particularly useful in the process because they undergo reaction with alkyl cyclopentanes to give a high proportion of desired products with a relatively small amount of undesirable side reactions. The olefin employed need not be entirely pure as any hydrocarbon fraction containing olefins may be utilized in the process. Thus a gas obtained from the cracking of oil and containing certain amounts of ethylene, propene and butenes can be utilized.

The hydrogen fluoride used as catalyst for the process of the present invention is preferably of at least 85% concentration. The remainder of the catalyst composite may comprise water and organic material added to or accumulated in the catalyst layer. When anhydrous, hydrogen fluoride is a liquid boiling at about 20° C. and accordingly it can be used in apparatus which is cooled to maintain temperatures below this point or it can be used as a liquid at higher temperatures but below the critical temperature if sufficient pressure is maintained upon the apparatus. The hydrogen fluoride catalyst is not readily changed by oxidation or reduction and if lost mechanically in the reaction product it can be recovered therefrom and re-used, while alkyl fluorides which are produced from olefins incidental to the alkylation are readily decomposable to recover therefrom hydrogen fluoride.

The details of operation of the present process are relatively simple since the cyclopentane hydrocarbons involved in the reactions are liquid at ordinary temperatures. According to the present invention, alkyl cyclopentanes are contacted with olefinic hydrocarbons in the presence of hydrogen fluoride catalyst under the desired conditions of temperature and pressure until the olefins have been substantially consumed and a substantially saturated hydrocarbon product is formed containing a relatively high proportion of alkyl cyclohexane hydrocarbons. In order to favor the alkylation reaction rather than olefin polymerization, a relatively higher molar proportion of alkyl cyclopentanes than olefins is maintained throughout the entire reaction. In some cases the molar ratio of methyl cyclopentane hydrocarbon to olefin may be approximately 1:1, while in other cases this ratio may be as high as 10:1 or more, the exact ratio being somewhat dependent upon the particular hydrocarbons charged. The ratio of alkyl cyclopentane to olefin hydrocarbons charged is subject to some variation and is affected considerably by the method of introducing the olefin-containing fraction and the efficiency of mixing.

It is characteristic of the present process that the isomerization-alkylation reactions predominate over the polymerization reaction of the olefins charged, even at pressures above atmospheric. The pressure at which the process is carried out will depend upon the temperature and thus atmospheric pressure may be used when operating at a temperature below the boiling point of the catalyst and reacting hydrocarbons. When higher temperatures are utilized, it is preferable to employ sufficient superatmospheric pressure to maintain in liquid state a substantial proportion of the reacting hydrocarbons and catalyst. Thus the temperature of the reaction may vary greatly depending upon the amount and concentration of the catalyst, the proportions and reactivities of the hydrocarbons involved, and other factors. The temperatures utilizable are generally between about −20° and about 200° C. while the preferred operating temperatures are from about 20° to about 120° C. It is advisable to carry out the reaction at as low a temperature as possible since at higher temperatures there is generally a marked increase in the rate of undesirable reactions which frequently result in decomposition and degradation of the desired products of the process.

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, alkylated cyclohexanes, higher boiling hydrocarbons, and catalyst; said complex mixture being withdrawn at substantially the same rate as that at which the hydrocarbon charging stocks and hydrogen fluoride catalyst are supplied to the alkylation reactor. The used hydrogen fluoride catalyst and unreacted alkyl cyclopentanes may be recycled to further treatment with olefins generally in the presence of some freshly-added hydrogen fluoride.

Batch type operation of the process is carried out by gradually introducing an olefin-containing fraction to a reaction vessel containing a mixture of the liquid alkyl cyclopentane and the hydrogen fluoride 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 isomerization and alkylation reactions, the used hydrogen fluoride catalyst layer is separated from the normally liquid hydrocarbon reaction mixture comprising essentially alkylated cyclohexane hydrocarbons and the excess of methyl cyclopentane hydrocarbons. The reaction mixture is separated by fractional distillation and the unconverted alkyl cyclopentane hydrocarbons are returned to further isomerization and alkylation treatment as hereinabove set forth.

The ratio of hydrogen fluoride catalyst to hydrocarbons in the reaction zone depends upon the operating temperature, pressure, type of hydrocarbons, etc. In general the ratio of liquid hydrogen fluoride catalyst to hydrocarbon mixture is usually 1:1 on a volume basis but this ratio may be varied from about 0.1:1 to about 2:1. The molar ratio of alkyl cyclopentane hydrocarbons to olefins will also vary, but it is preferred to have an excess of alkyl cyclopentane hydrocarbons in the reaction zone throughout the entire reaction. Pure alkyl cyclopentane hydrocarbons may be used as charging stock or hydrocarbon mixtures containing a substantial proportion of alkyl cyclopentanes such as some straight-run gasolines or other gasoline fractions containing naphthenic hydrocarbons. While pure olefins may sometimes be preferred as alkylating agents, cracked gases rich in the desired olefins may be employed similarly.

The process of the present invention may also be carried out in the presence of a catalyst comprising essentially a major proportion by weight

of hydrogen fluoride and a relatively minor proportion of boron fluoride. Under some conditions this mixed catalyst containing boron fluoride has a higher alkylating activity than hydrogen fluoride and thus permits more efficient interaction of methyl cyclopentanes with olefins particularly the lower-boiling normally gaseous olefins including ethylene.

The following example gives results obtained by the use of the present process, although it is not intended to limit the scope of the invention in exact correspondence with the example.

252 parts by weight of methyl cyclopentane and 157 parts by weight of liquid hydrogen fluoride catalyst (containing about 98% by weight of hydrogen fluoride and 2% water) were placed in an autoclave provided with a mechanical stirrer and inlet tube through which 126 parts by weight of a mixture of 1-butene and 2-butene was introduced gradually over a period of 3.5 hours while the reaction mixture was maintained at a temperature between 55° and 67° C. The reaction product was separated into a hydrocarbon layer and a hydrogen fluoride layer after which the hydrocarbon layer was washed with caustic soda solution and water and then was dried and distilled. The liquid hydrocarbon product obtained was found to contain 37.6% by volume of unreacted methyl cyclopentane, 17.7% of alkylated cyclohexanes, and 45% of higher boiling cyclic hydrocarbons.

The character of the present invention and its novelty and utility in producing alkylated cyclohexane hydrocarbons can be seen from the preceding specification and example given, 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 from alkyl cyclopentane hydrocarbons which comprises reacting an alkyl cyclopentane hydrocarbon with an olefinic hydrocarbon in the presence of a catalyst consisting essentially of hydrogen fluoride as its active ingredient.

2. A process for producing substantial yields of alkyl cyclohexane hydrocarbons from alkyl cyclopentane hydrocarbons which comprises reacting an alkyl cyclopentane hydrocarbon with an olefinic hydrocarbon in the presence of a catalyst consisting essentially of anhydrous hydrogen fluoride.

3. A process for producing substantial yields of alkyl cyclohexane hydrocarbons from alkyl cyclopentane hydrocarbons which comprises mixing an alkyl cyclopentane hydrocarbon, an olefinic hydrocarbon, and a catalyst containing at least 85% by weight of hydrogen fluoride as its essential active component and subjecting the resulting mixture to alkylating conditions such as to maintain the hydrocarbons and hydrogen fluoride substantially in liquid state.

4. A process for producing substantial yields of alkyl cyclohexane hydrocarbons from alkyl cyclopentane hydrocarbons which comprises reacting an alkyl cyclopentane hydrocarbon with an olefinic hydrocarbon at a temperature between about −20° and about 200° C. in the presence of a catalyst consisting essentially of hydrogen fluoride as its active ingredient.

5. A process for producing substantial yields of alkyl cyclohexane hydrocarbons from alkyl cyclopentane hydrocarbons which comprises mixing an alkyl cyclopentane hydrocarbon, an olefinic hydrocarbon, and a catalyst containing at least 85% of hydrogen fluoride and subjecting the resultant mixture to a temperature between about 20° and about 120° C. under a pressure sufficient to maintain the hydrocarbons and hydrogen fluoride substantially in liquid state.

6. The process of claim 3 further characterized in that the olefinic hydrocarbon comprises a normally gaseous olefin.

7. The process of claim 3 further characterized in that the olefinic hydrocarbon comprises a normally liquid olefin.

8. The process of claim 4 further characterized in that the alkyl cyclopentane hydrocarbon is maintained in molar excess to the olefinic hydrocarbon throughout the entire reaction.

9. A process for producing substantial yields of alkyl cyclohexane hydrocarbons from alkyl cyclopentane hydrocarbons which comprises reacting an alkyl cyclopentane hydrocarbon with a butene in the presence of a catalyst consisting essentially of hydrogen fluoride as its active ingredient.

10. A process for producing 1-ethyl-2,4-dimethyl cyclohexane which comprises reacting methyl cyclopentane with normal butene in the presence of a catalyst consisting essentially of hydrogen fluoride as its active ingredient.

11. A process for producing 1-ethyl-2,4-dimethyl cyclohexane which comprises reacting methyl cyclopentane with normal butene at a temperature between about 20° and about 120° C. in the presence of a catalyst containing at least 85% of hydrogen fluoride as its essential alkylating component.

12. 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 an olefin-containing hydrocarbon fraction at a temperature between about −20° and about 200° C. in the presence of a catalyst consisting essentially of hydrogen fluoride as its active ingredient.

13. 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 an olefin-containing hydrocarbon fraction at a temperature between about −20° and about 200° C. in the presence of a catalyst consisting essentially of hydrogen fluoride as its active ingredient while maintaining a molar excess of alkyl cyclopentanes to olefinic hydrocarbons throughout the entire reaction.

14. A continuous process for producing substantial yields of alkyl cyclohexane hydrocarbons from alkyl cyclopentane hydrocarbons which comprises continuously contacting an alkyl cyclopentane hydrocarbon with an olefinic hydrocarbon in a reaction zone maintained under alkylating conditions and while in admixture with an alkylation catalyst consisting essentially of hydrogen fluoride as its active ingredient, removing from said zone a reaction mixture of hydrocarbons and alkylation catalyst, separating said reaction mixture into a hydrocarbon layer and a catalyst layer, fractionating the hydrocarbon layer to separate alkyl cyclohexane hydrocarbons from recovered alkyl cyclopentane hydrocarbons, and returning at least a portion of said recovered alkyl cyclopentane hydrocarbons

and at least a portion of said catalyst layer to the reaction zone.

15. The process of claim 14 further characterized in that said olefinic hydrocarbon is a butene.

16. The process of claim 14 further characterized in that said alkyl cyclopentane hydrocarbons comprise methyl cyclopentane.

17. A process for synthesizing hydrocarbons which comprises reacting an alkyl cyclopentane hydrocarbon with an olefinic hydrocarbon in an alkylating zone at a temperature between about —20° and about 200° C. in the presence of a catalyst containing at least 85% by weight of hydrogen fluoride, removing from said zone a reaction mixture of hydrocarbons and catalyst, separating said reaction mixture into a hydrocarbon layer and a catalyst layer, fractionating the hydrocarbon layer to separate alkyl cyclohexane hydrocarbons from recovered alkyl cyclopentane hydrocarbons, and returning at least a portion of said recovered alkyl cyclopentane hydrocarbons and at least a portion of said catalyst layer to the reaction zone.

18. A process for synthesizing hydrocarbons which comprises reacting an alkyl cyclopentane hydrocarbon with an olefinic hydrocarbon in an alkylating zone at a temperature between about —20° and about 200° C. in the presence of a catalyst containing at least 85% by weight of hydrogen fluoride, removing from said zone a reaction mixture of hydrocarbons and catalyst, separating said reaction mixture into a hydrocarbon layer and a catalyst layer, fractionating the hydrocarbon layer to separate alkyl cyclohexane hydrocarbons from recovered alkyl cyclopentane hydrocarbons, returning at least a portion of said recovered alkyl cyclopentane hydrocarbons and at least a portion of said catalyst layer to the reaction zone, and subjecting said alkyl cyclohexane hydrocarbons to dehydrogenation to form a benzene hydrocarbon mixture containing substantial proportions of alkylated benzene hydrocarbons.

HERMAN PINES.
VLADIMIR N. IPATIEFF.