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CONVERSION OF HYDROCARBONS

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This application is a continuation-in-part of our co-pending application Serial No. 431,664 filed February 20, 1942.

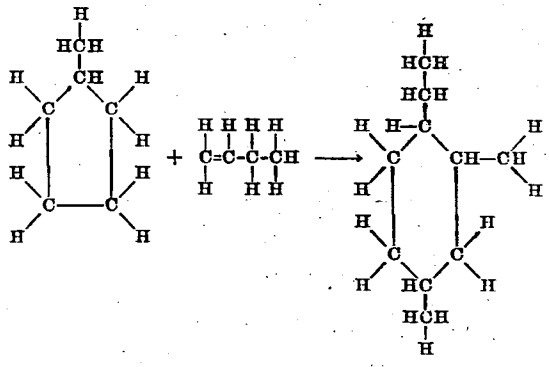
This invention relates particularly to a process for converting alkyl cyclopentanes into alkyl cyclohexanes by reacting the alkyl cyclopentanes with olefins in the presence of a catalyst.

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. Various alkylated naphthenic hydrocarbons can be illustrated by adding alkyl radicals to the base members of the respective series, such as, for example, cyclopentane, cyclohexane, etc. However, the actual synthesis of the various homologs does not follow such a simple mechanism as the reactions apparently involve a shifting of labile hydrogen atoms and a readjustment of valences. The naphthenes as a group include cycloparaffins of the general formula C_nH_{2n} and thus comprise hydrocarbons containing saturated ring structures.

The present process is particularly concerned with the 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 catalyst comprising essentially a major proportion by weight of hydrogen fluoride and a minor proportion of boron fluoride.

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 possible formation of certain proportions of intermediate addition compounds with 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 present invention than by isomerization alone. In this process the alkyl cyclopentanes are reacted with olefins in the presence of a mixture of hydrogen fluoride and boron fluoride. Under the preferred conditions 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 either before, after, or simultaneously with the alkylation reaction. By this process the alkylation and isomerization of alkyl cyclopentanes to alkyl cyclohexanes is accomplished rapidly and at a relatively low temperature such that undesirable side reactions are substantially prevented and the process is accordingly relatively easy to control.

Another advantage resides in the fact that nearly complete conversion of the alkyl cyclopentanes into the alkyl cyclohexanes can be obtained. The cyclohexane hydrocarbons so produced 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-boron 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 comprise ethylene and its higher homologs, both normally gaseous and normally liquid. Cyclo-olefins and polymers of normally gaseous olefins are also utilizable as alkylating agents. The normal butenes are particularly useful because they react with alkyl cyclopentanes to give high yields of desired products with relatively small amounts of unde-

sirable side reaction products. The different olefins employed need not be entirely pure as any hydrocarbon fraction containing an olefin may be utilized in the process. Thus a gas obtained from the cracking of oil and containing certain amounts of ethylene, propene, and butenes in addition to gaseous paraffins can be used for treating an alkyl cyclopentane to produce alkylated cyclohexane hydrocarbons.

The catalyst employed comprises essentially a mixture of hydrogen fluoride and boron fluoride and preferably consists of a major proportion of hydrogen fluoride and a minor proportion of boron fluoride. Hydrogen fluoride when anhydrous is a liquid boiling at about 20° C. under a pressure of 1 atmosphere, while boron fluoride, which is also referred to as boron trifluoride, is normally a gas with a boiling point of —101° C. and a melting point of —127° C. Boron fluoride can be commingled with hydrogen fluoride to form a catalyst mixture which can be used as a liquid in apparatus cooled to maintain a temperature somewhat below the boiling point of hydrogen fluoride or such a catalyst mixture can be used as a liquid at higher temperatures but below the critical temperature if sufficient pressure is maintained upon the apparatus. The catalyst is not readily changed by oxidation or reduction and if lost mechanically in the reaction product, it can be recovered therefrom and reused.

The details of operation 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 and boron fluoride catalyst under the desired conditions of temperature and pressure until the olefins have been substantially consumed and a 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 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 atmosphic 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 and practical 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 may be effected in either batch or continuous types of operation, it is usually carried out continuously by withdrawing from the reaction zone a complex mixture of excess unreacted alkyl cyclopentanes, alkylated cycylohexanes, 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-boron fluoride catalyst are supplied to the alkylation reactor. The used catalyst and unreacted alkyl cyclopentanes may be recycled to further treatment with olefins generally in the presence of some freshly added hydrogen fluoride-boron fluoride catalyst.

Batch type operation may be carried out by gradually introducing an olefin-containing fraction to a reaction vessel containing a mixture of the liquid alkyl cyclopentane 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 isomerization and alkylation reactions, the used 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-boron fluoride catalyst to hydrocarbons in the reaction zone depends upon the operating temperature, pressure, type of hydrocarbons, etc. In general the ratio of liquid catalyst mixture 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 following example indicates results obtainable although it is introduced with no intention to limit the scope of the invention.

Three molecular proportions of methyl cyclopentane and an equal liquid volume of a catalyst mixture consisting of 25% by weight of boron fluoride and 75% by weight of hydrogen fluoride of 98% concentration are placed under a liquefying pressure in an autoclave provided with a mechanically driven stirrer and an inlet tube through which 1 molecular proportion of propylene is introduced gradually over a period of

two hours while the reaction mixture is agitated and maintained at a temperature of between 30° and 50° C. The resultant reaction products are separated into a hydrocarbon mixture and a catalyst mixture after which the hydrocarbon mixture is washed with caustic soda solution and water and then dried and distilled. After separating the excess of unconverted methyl cyclopentane by distillation, a higher boiling reaction product is obtained consisting essentially of alkylated cyclohexane hydrocarbons. The recovered unconverted methyl cyclopentane and recovered hydrogen fluoride-boron fluoride catalyst are suitable for use in a further alkylation treatment.

The character of the 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 which comprises reacting an alkyl cyclopentane hydrocarbon and an olefinic hydrocarbon in the presence of a catalyst comprising essentially hydrogen fluoride and boron fluoride.

2. A process for producing substantial yields of alkyl cyclohexane hydrocarbons which comprises mixing an alkyl cyclopentane hydrocarbon, an olefinic hydrocarbon, and a catalyst comprising essentially hydrogen fluoride and boron fluoride, and subjecting the resultant mixture to alkylating conditions such as to maintain the hydrocarbons and catalyst in substantially liquid state.

3. A process for producing substantial yields of alkyl cyclohexane hydrocarbons which comprises reacting an alkyl cyclopentane hydrocarbon and an olefinic hydrocarbon at a temperature of from about —20° to about 200° C. in the presence of a catalyst comprising essentially hydrogen fluoride and boron fluoride.

4. A process for producing substantial yields of alkyl cyclohexane hydrocarbons which comprises mixing an alkyl cyclopentane hydrocarbon, an olefinic hydrocarbon, and a catalyst comprising essentially hydrogen fluoride and boron fluoride, and subjecting the resultant mixture to alkylation at a temperature of from about —20° to about 120° C.

5. The process of claim 3 further characterized in that said alkyl cyclopentane hydrocarbon is maintained in substantial molar excess to the olefinic hydrocarbon through the entire reaction.

6. A process for producing substantial yields of alkyl cyclohexane hydrocarbons which comprises reacting an alkyl cyclopentane hydrocarbon with propene in the presence of a catalyst comprising essentially hydrogen fluoride and boron fluoride.

7. A process for treating a gasoline boiling range hydrocarbon fraction containing alkyl cyclopentane hydrocarbons to produce alkyl cyclohexane hydrocarbons 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 comprising essentially hydrogen fluoride and boron fluoride.

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

9. A process for synthesizing hydrocarbons which comprises reacting an alkyl cyclopentane hydrocarbon with an olefinic hydrocarbon in an alkylating zone at a temperature of from about —20° to about 200° C. in the presence of a catalyst comprising essentially a major proportion by weight of hydrogen fluoride and a relatively minor proportion by weight of boron fluoride, removing from said zone a reaction mixture of hydrocarbons and catalyst, separating said reaction mixture into a hydrocarbon mixture and a catalyst mixture, fractionating the hydrocarbon mixture to separate alkyl cyclohexane hydrocarbons from recovered alkyl cyclopentane hydrocarbon, and returning at least a portion of said recovered alkyl cyclopentane hydrocarbon and at least a portion of said catalyst mixture to the reaction zone.

10. A process for synthesizing hydrocarbons which comprises reacting an alkyl cyclopentane hydrocarbon with an olefinic hydrocarbon in an alkylating zone at a temperature of from about —20° to about 200° C. in the presence of a catalyst comprising essentially a major proportion by weight of hydrogen fluoride and a relatively minor proportion by weight of boron fluoride, removing from said zone a reaction mixture of hydrocarbons and catalyst, separating said reaction mixture into a hydrocarbon mixture and a catalyst mixture, fractionating the hydrocarbon mixture to separate alkyl cyclohexane hydrocarbons from recovered alkyl cyclopentane hydrocarbon, returning at least a portion of said recovered alkyl cyclopentane hydrocarbon and at least a portion of said catalyst mixture 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.

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

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

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