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HYDROCARBON REACTIONS

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This invention is more particularly related to reactions which occur between relatively stable cyclic hydrocarbons comprising benzol and its homologs and the members of the relatively unstable group of cycloparaffins having less than 5 carbon atoms in the ring.

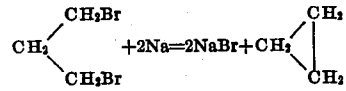
More specifically the invention is concerned with catalytic processes which enable the production of higher molecular weight alkylated derivatives of mono nuclear aromatics by the addition of alkyl groups through the agency of the designated unstable cycloparaffins.

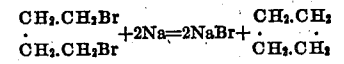
The art of synthesizing organic compounds and particularly those of a hydrocarbon character with which the present invention is concerned is important in view of the fact that special hydrocarbons in any one series may have peculiar characteristics rendering them suitable for use either as a basis for the development of useful derivatives or direct use in hydrocarbon mixtures such as, for example, those employed as fuels for internal combustion engines, lubricants etc. and the present invention is a contribution to the art of catalytically synthesizing such hydrocarbons.

In one specific embodiment the invention comprises a process for the treatment of relatively stable hydrocarbons comprising benzol and its homologs with cycloparaffins containing 3 and 4 carbon atoms in the ring and comprising cyclopropane and cyclobutane to form alkylated derivatives of said stable hydrocarbons while utilizing relatively concentrated sulfuric acid catalysts, and relatively low temperature conditions.

The aromatic hydrocarbons which may be alkylated by the low molecular weight cycloparaffins according to the present process comprise benzol as the simplest member of the series and any of its higher homologs which are still capable of adding more alkyl groups. This does not necessarily infer that all homologs are equally reactive or that all those containing unsubstituted ring hydrogen atoms are capable of further alkylation since the possibility of adding further alkyl groups is one determinable only by experiment.

The cyclopropane and cyclobutane necessary for the process may be produced by the action of sodium on dihalogen derivatives of propane and n-butane respectively in which the halogen substitution is on the end carbon atoms. The reactions of this method of formation are shown in the following equations.





Other methods of manufacture may be employed involving various types of condensation and cyclization reactions although the above is generally the simplest and most practical. The principal properties of the two cycloparaffins are given below:

Compound	Boiling point, ° C.	Specific gravity at 4° C.
Cyclopropane	−35	
Cyclobutane	11–12	0.7038

Since the two cycloparaffinic compounds shown above are gaseous at ordinary temperatures, the methods of operation whereby they are used to alkylate aromatic hydrocarbons are relatively simple and consist generally in passing cyclopropane or cyclobutane or a mixture of the two into well stirred mixtures of aromatic hydrocarbons and sulfuric acid, the temperature preferably being maintained within the approximate range of −10 to +30° C. and the acid concentration being preferably above 85%. While a certain degree of sulfonation of the aromatics may take place primarily, there is no particular disadvantage in this since the introduction of the cycloparaffins results in the alkylation of the aromatics with the regeneration of sulfuric acid for further use in the reactions. In the case of cyclobutane and its alkylated derivatives such as methyl cyclobutane which may be normally liquid or readily liquefiable in the preferred temperature range, the operation may be modified by mixing the cycloparaffin and the aromatic with the proper proportion of sulfuric acid and maintaining the components of the mixture in intimate contact by mechanical stirring for a definite period of time with outside cooling to prevent undue temperature rise. After any of

these treatments the acid and hydrocarbon layers are separated and the latter subjected to fractionation for the recovery of individual compounds or close cuts. Obviously operations may be conducted either in batch or continuous systems. The alkylated products may be washed with caustic soda or other alkalis to remove traces of acids or acid products of the reactions and the spent acid catalyst may be treated by any necessary method to restore it to the condition fitting it for further service.

The present process is particularly applicable to the treatment of the light distillate produced in the destructive distillation of coal and other hydrocarbonaceous material. It is also applicable to the treatment of analogous highly aromatic distillates produced by the intensive cracking of the heavier portions of petroleum to produce gasoline or by the reforming or secondary cracking of primary gasoline distillates, since definite percentages of aromatics are formed by the intensive cracking of practically all types of hydrocarbons. The alkylation of such aromatic distillates evidently involves principally the addition of propyl and butyl radicals formed by the opening of the 3 and 4 carbon atom cycloparaffins although other secondary reactions may occur leading to the formation of alkyl groups having a lesser or a greater number of carbon atoms.

It is a feature of the present process that the alkyl derivatives of aromatics formed by reacting them with cyclopropane or cyclobutane are predominantly of a normal character as distinguished from similar derivatives made by using propylene and butylene. The mechanism of the reactions which lead to the formation of the normal alkyl derivatives is not known but it may be safely stated that the present process forms a definite means of producing such normal aromatic derivatives.

The temperatures of operation are maintained at a relatively low point so that ordinarily temperatures of above 30° C. are seldom utilized unless the aromatic or mixture of aromatics undergoing treatment is solid at these temperatures when more elevated temperatures may be used above their melting points and also if desired somewhat less reactive catalysts corresponding to the more dilute acid.

The following examples are given to indicate the type of reactions involved in the process of the present invention although not with the intention of unduly limiting its proper scope.

Example I

Into a solution of approximately 90 parts by weight of benzene and 45 parts by weight of 96% sulfuric acid maintained at a temperature of approximately 5° C., 18 parts by weight of cyclopropane were passed at atmospheric pressure over a period of approximately 1 hour. The hydrocarbon layer was then separated and further treated by washing with cold 96% sulfuric acid followed by water, dilute caustic, and a final water wash. A yield of normal propyl benzene boiling at 150 to 157° C. was obtained in an amount corresponding to approximately 35% of the theoretical.

Example II

A mixture of 30 parts by weight of methyl cyclobutane, 90 parts by weight of benzene and 90 parts by weight of 96% sulfuric acid was maintained at a temperature of approximately 4° C. for a period of 2½ hours during which time the materials were vigorously agitated. After separation of the hydrocarbon layer, it was washed with cold 96% sulfuric acid, followed by water, dilute caustic soda, and a final water wash. In this case a yield of approximately 30% of material corresponding in its properties to a mixture of amyl benzenes was separated.

The nature of the present invention and its practical possibilities are evident from the foregoing description and numerical data, neither of which however is intended to unduly limit its proper scope.

We claim as our invention:

1. A process for producing alkylated aromatics which comprises reacting an aromatic with a cycloparaffin of less than 5 carbon atoms in the ring in the presence of sulphuric acid.

2. A process for producing alkylated aromatics which comprises reacting an aromatic with a cycloparaffin of less than 5 carbon atoms in the ring in the presence of sulphuric acid and at a temperature of from −10 to +30° C.

3. A process for producing alkylated aromatics which comprises reacting an aromatic with a cycloparaffin of less than 5 carbon atoms in the ring in the presence of sulphuric acid of above 85% concentration and at a temperature of from −10 to +30° C.

4. A process for producing normal propyl derivatives of aromatic hydrocarbons which comprises subjecting said hydrocarbons to the action of cyclo-propane at temperatures of the order of −10 to +30° C. in the presence of sulfuric acid of over 85% concentration.

5. A process for producing normal butyl derivatives of aromatic hydrocarbons which comprises subjecting said hydrocarbons to the action of cyclo-butane at temperatures of the order of −10 to +30° C. in the presence of sulfuric acid of over 85% concentration.

6. A process for producing normal propyl benzene which comprises subjecting said benzene to the action of cyclo-propane at temperatures of the order of −10 to +30° C. in the presence of sulfuric acid of over 85% concentration.

7. A process for producing normal butyl benzene which comprises subjecting said benzene to the action of cyclo-butane at temperatures of the order of −10 to +30° C. in the presence of sulfuric acid of over 85% concentration.

8. A process for producing amyl benzenes which comprises subjecting benzene to the action of methyl cyclo-butane at temperatures of the order of −10 to +30° C. in the presence of sulfuric acid of over 85% concentration.

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