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ALKYLATION OF AROMATIC HYDROCARBONS WITH ISOPARAFFINS

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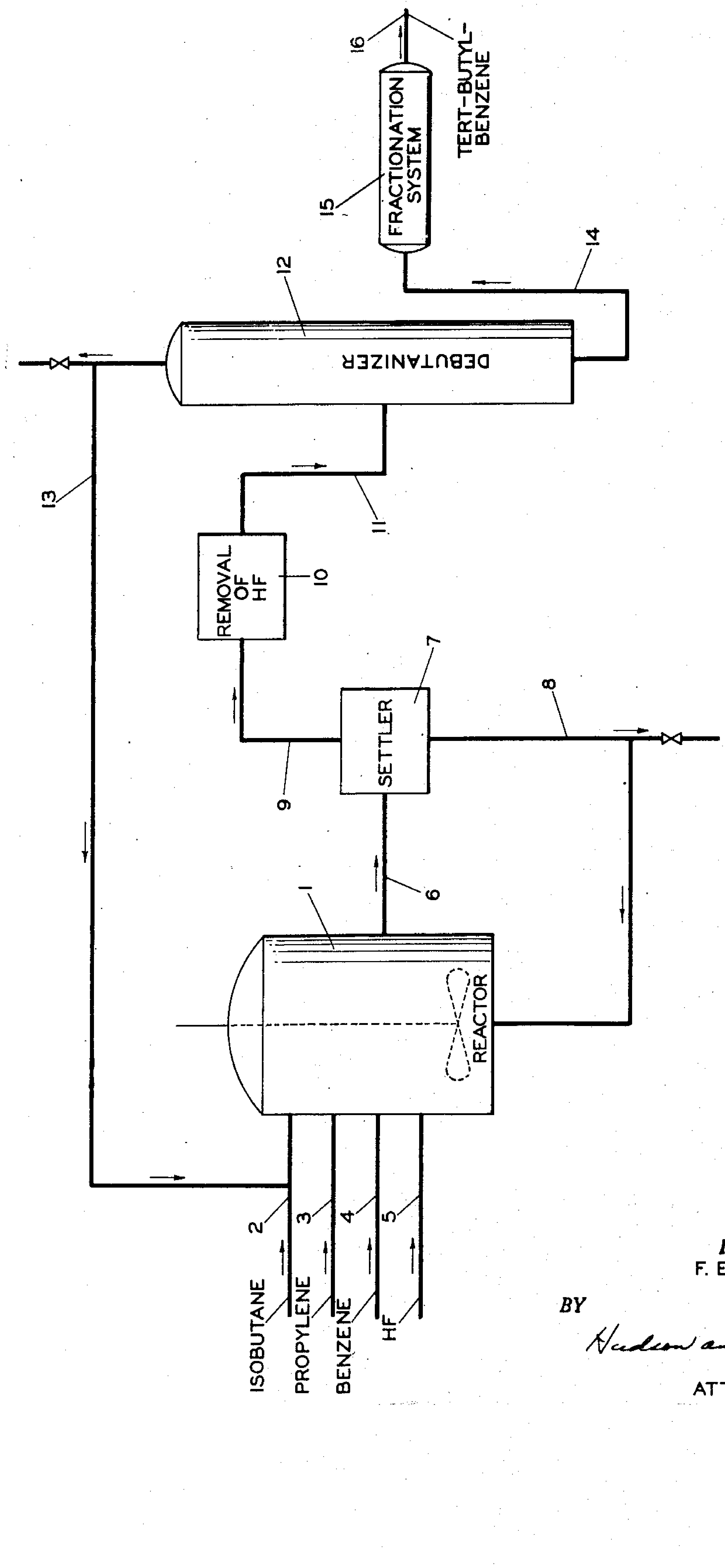

INVENTOR.
F. E. CONDON

BY
Hudson and Young
ATTORNEYS

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ALKYLATION OF AROMATIC HYDROCARBONS WITH ISOPARAFFINS

Francis E. Condon, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

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The present invention relates to a method of accomplishing the alkylation of aromatic hydrocarbons with isoparaffins, i. e. the introduction on a ring carbon atom of an alkyl group derived from and having the structure of an isoparaffin.

The alkylated aromatic hydrocarbons are of great commercial importance. They are especially valuable for blending in motor and aviation gasoline and as solvents and chemical intermediates. Previously they have been made predominantly or exclusively by the alkylation of the aromatic hydrocarbon with an aliphatic olefin or an alkyl halide or an aliphatic alcohol.

The principal object of the present invention is to provide a method for the alkylation of aromatic hydrocarbons with isoparaffins. Another object is to provide an improved method of making alkylbenzenes, especially tertiary alkyl benzenes, for example, tertiary butyl benzene.

Another object is to make available a process for the alkylation of aromatic hydrocarbons with isobutane as a tertiary butylating agent. Numerous other objects will more fully hereinafter appear.

The accompanying drawing portrays diagrammatically one arrangement of equipment and flow which may be employed for carrying out the present invention in one typical embodiment thereof.

I have now discovered that aromatic hydrocarbons can be alkylated with isoparaffins by subjecting a mixture of the aromatic hydrocarbon, an isoparaffin, an aliphatic olefin and an alkylation catalyst to reaction conditions such that the aromatic hydrocarbon is alkylated with the olefin. My invention is based on the discovery that when such a process is conducted, concomitant alkylation of the aromatic hydrocarbon with an alkyl group derived from and having the structure of the isoparaffin is accomplished.

The temperature at which the reaction is conducted is preferably substantially atmospheric. Moderate temperatures ranging from 20 to 30° C. are very suitable for carrying out the present invention and are preferred. However, temperatures ranging from 0° C. to as high as 50° C. may be employed.

The time of reaction should be sufficient to bring the reaction substantially to equilibrium. Usually the reaction time will be at least 5 minutes and not over 1 hour. Reaction times of the order of 5 to 15 minutes are often adequate. The time should be as short as possible in order to give maximum output from equipment of a given size.

Any suitable liquid alkylation catalyst which is capable of effecting alkylation of the aromatic with the olefin under conditions herein described

may be employed. Generally speaking, I employ the liquid inorganic acids which have been used heretofore for alkylating isoparaffins with aliphatic olefins. These acids are substantially anhydrous hydrofluoric acid and concentrated sulfuric acid. Hydrofluoric acid is by far preferred for the practice of my invention.

The alkylation yields not only the alkyl benzenes formed by alkylation of the aromatic with the olefin but also alkyl benzenes wherein the alkyl substituent is derived from and has the structure of the isoparaffin employed.

The term "isoparaffin" is used herein with its usual meaning, i. e. to denote any branched chain paraffin hydrocarbon. This term has been heretofore used in at least two different ways, namely to denote (1) the 2-methyl alkanes; for example isobutane (2-methyl propane), isopentane (2-methyl butane), isohexane (2-methyl pentane) and so on through the paraffin series and (2) the branched chain paraffins generally. I use it in the second sense. In addition to these two meanings the term "isooctane" has had an additional meaning since it has been employed to designate the specific branched chain octane 2,2,4-trimethyl pentane. The number of carbon atoms per molecule in the isoparaffin may range from 4 upwardly to any desired number, say 10 or even 20 or higher. Generally the isoparaffin will not have more than 8 carbon atoms per molecule. More commonly the isoparaffin will be isobutane or isopentane since these are readily available and since the corresponding alkyl benzenes are more in demand under present conditions.

It should be pointed out, however, that the term "isopentane" is used herein with its usual meaning, i. e. to denote 2-methyl butane.

The pressure maintained in the reaction zone should be such as to hold all of the ingredients present in the reaction zone in the liquid phase.

The amount of catalyst employed may vary within fairly wide limits. Preferably it will be at least equal to the amount of hydrocarbon or organic phase present in the reaction zone. In general the ratio of catalyst to hydrocarbon charge should be from 2:1 to 1:2 by volume. A ratio of about 1:1 will commonly be employed.

The concentration of aromatic hydrocarbon in the hydrocarbon feed to the reaction zone is preferably less than 10 per cent by weight and more preferably not over 2 per cent by weight.

The concentration of olefin in the hydrocarbon charge preferably ranges from 0.5 to 2 molecular equivalents per molecular equivalent of aromatic hydrocarbon present.

The molecular ratio of isoparaffin to aromatic hydrocarbon in the reaction zone is generally between 10 and 1000. A ratio of at least 50 is preferred.

Any alkylatable aromatic hydrocarbon may be employed in the practice of my invention. Generally I prefer to use the monocyclic aromatics such as benzene, toluene, xylene, ethylbenzene, isopropyl benzene, etc. However, I may use the polycyclic aromatics such as naphthalene.

The reaction zone should be equipped with means for agitating the contents thereof vigorously so as to produce the desired intimacy of contact between the immiscible catalyst phase and the hydrocarbon phase. The reaction zone should also be provided with means for maintaining the proper temperature therein. Any suitable contacting equipment may be used, such as that commonly employed for carrying out the alkylation of isoparaffins with aliphatic olefins at moderate temperatures and pressure.

Generally speaking, the reaction conditions are such that the predominant reaction is alkylation of the aromatic hydrocarbon with the olefin to produce the corresponding alkylated aromatic and that an important though lesser reaction is the concomitant alkylation of the aromatic with an alkyl group corresponding to and derived from the isoparaffin.

In accordance with this invention, a mixture comprising an isoparaffin to be used as alkylating agent, for example, isobutane if tertiary butylation is desired, an aromatic hydrocarbon to be alkylated, for example, benzene, and an aliphatic olefin (preferably one having a different number of carbon atoms than the isoparaffin to be used as alkylating agent), for example, propylene, is subjected to the action of an alkylating catalyst, which may suitably be hydrofluoric acid, at a convenient temperature which need not differ appreciably from ordinary room temperature (25° C.) and for a suitable period of time which may conveniently be of the order of 5 to 15 minutes. Operation may suitably be continuous with recycling of the catalyst.

The catalyst-free effluent is then freed of unchanged isoparaffin (which must, for the most successful operation of this process, be present in large excess), suitably by distillation.

The alkylation product will contain alkyl benzenes derived from alkylation of the benzene with the olefin used, i. e. those alkyl benzenes that would be obtained in the absence of isoparaffin. But also, there will be present an appreciable amount of alkyl benzenes derived from and therefore having an alkyl group with the structure of the isoparaffin used. For example, a considerable amount of tertiary butyl benzene will be found in the alkylate from an isobutane-benzene-propylene mixture. The yield of aromatic alkylation product derived from isoparaffin will be greater, the greater is the ratio of isoparaffin to aromatic hydrocarbon in the feed. Thus, a preferred method of operating consists in using less than 10 per cent by weight of aromatic hydrocarbon in the charge mixture. The percentage yield of aromatic alkylation product derived from the isoparaffin will be increased still further, however, as the percentage of aromatic hydrocarbon in the feed is decreased, so that a concentration of 2 per cent by weight or aromatic hydrocarbon is better than a concentration of 10 per cent by weight. Lower concentrations result in an even greater percentage of aromatic alkylate derived from the isoparaffin, but the penalty of having to free the effluent from a greater amount of unchanged isoparaffin becomes greater. Generally, the concentration of olefin in the charge is maintained approximately molecularly equivalent to the amount of aromatic hydrocarbon, although varying this from 0.5 molecular equivalent to 2 molecular equivalents of olefin per molecular equivalent of aromatic should not have any adverse effect on the percentage of aromatic alkylate derived from the isoparaffin. Thus, the use of feeds in which the molecular ratio of isoparaffin to aromatic hydrocarbon is between 10 and 1000 and preferably is at least 50, and the molecular ratio of aromatic hydrocarbon to olefinic hydrocarbon is between 0.5 and 2.0, for the purpose of obtaining alkyl benzenes derived from the isoparaffin, is within the scope of the present invention.

While the preceding discussion, and the examples, refer specifically to a mixture of isobutane, benzene and propylene, in which case the alkyl benzenes derived from the isoparaffin consist of tertiary butyl benzene, di-(tertiary butyl) benzene and tertiary butyl isopropyl benzenes, the use of other mixtures of an analogous nature is not beyond the scope of the present invention. The use of isopentane, for example, instead of isobutane, when the production of tertiary amyl benzenes is desired, is an obvious variation of the present process. The use of olefins other than propylene, for example, the use of butylenes when isopentane is the paraffin used, is an entirely feasible variation of the present process. Preferably, however, the olefin used has a number of carbon atoms different from that of the isoparaffin used, in order to facilitate separation, by fractional distillation, of the alkyl benzenes derived from the olefin from those derived from the isoparaffin.

The process of the present invention is conducted under substantially anhydrous conditions i. e. in the presence of not more than a trace of water. This may be accomplished by using commercially available anhydrous hydrofluoric acid, by dehydrating the hydrocarbon feeds in the usual way and by taking ordinary precautions to exclude water from access to the reaction zone as by using conventional closed pressure-resisting contactor and subsequent pieces of equipment.

In the discussion and in the examples, hydrofluoric acid is used as the catalyst for bringing about aromatic alkylation by isoparaffins. However, it will be obvious to one skilled in the art that other alkylating catalysts may produce the same result. For example, concentrated sulfuric acid, aluminum chloride, or various modified forms of aluminum chloride, which are generally known to be useful alkylating catalysts, may be used instead of hydrofluoric acid for the production of alkylbenzenes derived from isoparaffins in mixtures of isoparaffins, olefins, and aromatic hydrocarbons. However I prefer to use substantially anhydrous hydrofluoric acid.

In all applications, however, the use of a high molecular ratio of isoparaffin to aromatic hydrocarbon, i. e. at least 10:1 and preferably at least 50:1, in order to increase the percentage of alkylated aromatic hydrocarbons derived from the isoparaffin, is to be considered an optimus modus operandi, and a principle which is herewith disclosed for the first time.

A second novel principle herewith disclosed for the first time, is the necessity of an olefin (or its chemical equivalent) in order to bring about aromatic alkylation by an isoparaffin under the mild conditions of temperature and contact time used in the present process. Thus it is well known that isobutane in the absence of olefins will not alkylate benzene under the mild conditions here specified as preferable: namely, (1) the use of hydrofluoric acid as a catalyst; (2) a temperature near 25° C.; (3) a contact time of 5 to 15 minutes. The function of the olefin may be to remove hydrogen from the isoparaffin, thus converting it to an olefin, which then alkylates the aromatic hydrocarbon. A corresponding amount of olefin would then be expected to be hydrogenated to its corresponding paraffin hydrocarbon.

Since, in the presence of hydrofluoric acid, alkyl fluorides exhibit the same chemical behavior as their parent olefins in many alkylation reactions, it is to be expected that an alkyl fluoride may function as well as an olefin to bring about aromatic alkylation by an isoparaffin in a mixture of alkyl fluoride, isoparaffin, and aromatic hydrocarbon with hydrofluoric acid as a catalyst. Similarly, if an aluminum chloride catalyst is used, an alkyl chloride would be expected to function as well as its parent olefin in promoting aromatic alkylation by an isoparaffin. Therefore the alkyl halides are believed to be substantial equivalents of aliphatic olefins for the practice of the present invention. However, in general, I prefer to employ the olefins rather than the alkyl halides.

Examples

Two runs are described in which blends of isobutane, benzene and propylene were pumped into a 1470 ml. copper-plated steel reactor where they were intimately mixed with substantially anhydrous hydrofluoric acid. The acid-hydrocarbon emulsion so produced passed to a settler, from which substantially hydrocarbon-free acid was recycled to the reactor, and substantially acid-free hydrocarbon was collected in a large receiver. In the reactor, the acid-to-hydrocarbon ratio was maintained near unity, by addition of small amounts of fresh acid when necessary. The reactor was surrounded by a stirred water bath for maintenance of temperature. The effluent hydrocarbon was washed with water to remove traces of acid, and the excess isobutane was removed in a 10-foot corrosion-resistant metal fractionating column 1¼ inches in diameter packed with ¼-inch Raschig rings. Butane-free alkylate was analyzed by fractional distillation in glass columns. The pertinent data are presented in the table.

TABLE

	Example 1	Example 2
Operating conditions:		
Temperature, °F	90	92
Pressure, p. s. i	160	180
Contact time, minutes	11.8	6.7
Isobutane/propylene (mole ratio)	11.1	70.4
Benzene/propylene (mole ratio)	0.9	1.1
Isobutane/benzene (mole ratio)	12.8	63.6
Composition of Feed, wt. percent:		
Propane	0.3	0.3
Propylene	5.1	1.0
Isobutane	83.3	95.5
Normal butane	2.6	1.2
Benzene	8.7	2.0
Composition of Butane-free alkylate, vol. percent:		
Isoparaffins	4.3	8.0
Benzene	12.2	19.7
Isopropylbenzene	36.5	35.4
tert-butylbenzene	3.0	6.7
Diisopropylbenzenes	34.0	25.4
tert-butylisopropylbenzenes		
Di-(tert-butyl) benzenes		
Heavier	10.0	4.8

Comparison of the data of Examples 1 and 2 shows that a five-fold increase in the mole-ratio of isobutane to benzene served to more than double the percentage of tertiary-butylbenzene in the butane-free alkylate.

In the drawing, isobutane, propylene, benzene and HF in suitable proportions are fed to reactor **1** via lines **2**, **3**, **4** and **5**, respectively. These materials may of course be admixed prior to introduction to reactor **1**. The reaction effluent passes via line **6** to settler **7** where it separates into an acid phase and a hydrocarbon phase. The acid phase may be recycled in part or in toto to vessel **1** by means of line **8**. If desired, a suitable portion of the acid phase may be withdrawn from the recycle circuit. The withdrawn acid phase may be passed to a suitable recovery or re-run system in amount such as to keep activity of the acid catalyst in the system at the proper level and to keep impurities therein from building up to an objectionable level. The hydrocarbon phase may be passed via line **9** to unit **10** wherein HF is removed in any suitable way. The hydrocarbon stream is then fed via line **11** to debutanizer **12** which removes the unreacted isobutane and any normal butane overhead. This overhead may be recycled to reactor **2** via line **13**. If desired a suitable portion may be withdrawn from the system as indicated. Propane may be removed in admixture with the butane at this point or may have been removed in admixture with HF in unit **10**. If desired unit **10** may be eliminated and the free HF may be removed overhead in column **12** in admixture with propane and butanes, the resulting fraction being recycled in whole or in part to reactor **2** via line **13**. The bottoms fraction from column **12** is fed via line **14** to fractionation system **15** wherein it is resolved into any desired fractions, as a fraction of tertiary butylbenzene removed via line **16**. Other fractions such as isoparaffins above isobutane, benzene, isopropylbenzene, etc. may be recovered by means of the system **15**.

From the foregoing description it will be seen that the present invention makes possible a hitherto unknown reaction, namely the alkylation of aromatic hydrocarbons with an isoparaffin to give an alkylated aromatic wherein the alkyl group is derived from and corresponds to said isoparaffin. This is highly advantageous and so far as I am aware has not heretofore been thought possible. Another advantage is that the reaction takes place under moderate conditions of temperature and pressure and can be carried out in equipment which is readily available. Another advantage is that the process affords a simple and economical way of making alkylated aromatic hydrocarbons wherein the alkyl group substituent on the nuclear carbon atom or atoms is derived from an isoparaffin.

I claim:

1. The process of alkylating an aromatic hydrocarbon which comprises subjecting a hydrocarbon mixture in which the reactive components consist essentially of an aromatic hydrocarbon, an isoparaffin having 4 to 20 carbon atoms per molecule and an aliphatic olefin, having a skeletal configuration different from that of the isoparaffin, in admixture with an alkylation catalyst consisting of substantially anhydrous hydrofluoric acid, the molecular ratio of said isoparaffin to said aromatic hydrocarbon being at least 10:1, the molecular ratio of said aromatic hydrocarbon to said olefin being between 0.5:1 and 2.0:1 to a reaction temperature of from

20 to 30° C. for a reaction time of at least 5 minutes but not over one hour and under a pressure such as to maintain the materials present in the liquid phase, whereby said aromatic hydrocarbon is alkylated with said olefin and is concomitantly alkylated with an alkyl group derived from and having the skeletal structure of said isoparaffin and recovering said aromatic hydrocarbon alkylated with said alkyl group derived from and having the skeletal structure of said isoparaffin as the product of the process.

2. The process of alkylating an aromatic hydrocarbon which comprises subjecting a hydrocarbon mixture in which the reactive components consist essentially of an aromatic hydrocarbon, an isoparaffin having 4 to 20 carbon atoms per molecule and an aliphatic olefin, having a skeletal configuration different from that of the isoparaffin, in admixture with an alkylation catalyst consisting essentially of anhydrous hydrofluoric acid, the molecular ratio of said isoparaffin to said aromatic hydrocarbon being at least 50:1, the molecular ratio of said aromatic hydrocarbon to said olefin being between 0.5:1 and 2.0:1, to a temperature of from 20 to 30° C. for a reaction time of at least 5 minutes but not over 15 minutes, whereby said aromatic hydrocarbon is alkylated with said olefin and is concomitantly alkylated with an alkyl group derived from and having the skeletal structure of said isoparaffin and recovering said aromatic hydrocarbon alkylated with said alkyl group derived from and having the skeletal structure of said isoparaffin as the product of the process.

3. The process of alkylating benzene with isobutane which comprises subjecting a hydrocarbon mixture in which the reactive components consist essentially of benzene, isobutane and an aliphatic olefin having a different number of carbon atoms per molecule from isobutane in admixture with an alkylation catalyst consisting of substantially anhydrous hydrofluoric acid to a reaction temperature of from 20 to 30° C. for a period of time of at least 5 minutes and not over one hour, the molecular ratio of said isobutane to said benzene being at least 10:1 but not greater than 1000:1, the molecular ratio of said benzene to said olefin being between 0.5:1 and 2.0:1 the reaction pressure being such as to hold the components in the liquid phase, whereby said benzene is alkylated with a tertiary butyl group derived from said isobutane concomitantly with the alkylation of said benzene with said olefin and recovering said benzene alkylated with a tert-butyl group as a product of the process.

4. The process of alkylating benzene with isobutane which comprises subjecting a hydrocarbon mixture in which the reactive components consist essentially of benzene, isobutane and propylene in admixture with an alkylation catalyst consisting essentially of anhydrous hydrofluoric acid, the molecular ratio of said isobutane to said benzene being at least 50:1 and the molecular ratio of said benzene to said propylene being between 0.5:1 and 2.0:1, to a reaction temperature of from 20 to 30° C. for a reaction time of from 5 to 15 minutes under a pressure sufficient to hold the components in liquid phase and thereby effecting alkylation of said benzene with a tertiary butyl group derived from said isobutane concomitantly with alkylation of said benzene with said propylene and recovering said benzene alkylated with a tert-butyl group as a product of the process.

5. The process of alkylating benzene with isobutane to give tertiary butyl benzene which comprises subjecting a hydrocarbon mixture in which the reactive components consist of benzene, isobutane and propylene in admixture with an alkylation catalyst consisting of substantially anhydrous hydrofluoric acid, the molecular ratio of said isobutane to said benzene being approximately 63.6:1 and the molecular ratio of said benzene to said propylene being approximately 1:1, the acid-hydrocarbon ratio being maintained at approximately unity, to a temperature of approximately 92° F. for a contact time of approximately 6.7 minutes and a pressure of approximately 180 pounds per square inch gauge while subjecting the mixture to agitation to produce intimate contact between the acid and the hydrocarbon phases, and thereby effecting simultaneous alkylation of said benzene with a tertiary butyl group derived from said isobutane and alkylation of said benzene with said propylene, withdrawing the resulting mixture and causing same to separate into an acid phase and a hydrocarbon phase, and recovering tertiary butyl benzene from said hydrocarbon phase.

6. The process of alkylating an aromatic hydrocarbon which comprises subjecting a hydrocarbon mixture in which the reactive components comprise an aromatic hydrocarbon, an isoparaffin having 4 to 20 carbon atoms per molecule and an aliphatic olefin, having a skeletal configuration different from that of the isoparaffin, in admixture with an alkylation catalyst comprising hydrofluoric acid, the molecular ratio of said isoparaffin to said aromatic hydrocarbon being at least 10:1, the molecular ratio of said aromatic hydrocarbon to said olefin being between 0.5:1 and 2.0:1, to a reaction temperature in the range between 0° and 50° C. for a reaction time of at least five minutes but not over one hour and under a pressure such as to maintain a liquid phase, whereby said aromatic hydrocarbon is alkylated with said olefin and is concomitantly alkylated with an alkyl group derived from and having the skeletal structure of isoparaffin and recovering said aromatic hydrocarbon alkylated with an alkyl group derived from and having the skeletal structure of said isoparaffin as a product of the process.

7. The process of alkylating an aromatic hydrocarbon which comprises subjecting a hydrocarbon mixture in which the reactive components consist essentially of an aromatic hydrocarbon, an isoparaffin having 4 to 20 carbon atoms per molecule and an aliphatic olefin, having a skeletal configuration different from that of the isoparaffin, in admixture with an alkylation catalyst consisting essentially of anhydrous hydrofluoric acid, the molecular ratio of said isoparaffin to said aromatic hydrocarbon being at least 50:1, the molecular ratio of said aromatic hydrocarbon to said olefin being between 0.5:1 and 2.0:1, to a temperature of from 0° to 50° C. for a reaction time of at least 5 minutes but not over 15 minutes, whereby said aromatic hydrocarbon is alkylated with said olefin and is concomitantly alkylated with an alkyl group derived from and having the skeletal structure of said isoparaffin and recovering said aromatic hydrocarbon alkylated with an alkyl group derived from having the skeletal structure of said isoparaffin as a product of the process.

FRANCIS E. CONDON.

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