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TREATMENT OF HYDROCARBONS

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This invention relates particularly to the treatment of aromatic hydrocarbons to produce higher molecular weight alkyl derivatives thereof. More specifically, the process is concerned with a method of alkylating aromatics by the fragments of aliphatic hydrocarbon molecules produced by the dissociation reactions concurrent with their addition to the aromatic rings.

It is recognized that in general the alkylation of aromatic hydrocarbons with olefinic hydrocarbons has been known for a considerable time, particularly when employing sulfuric acid as a catalyst to further the reactions. However, the present invention differentiates from previous art on this subject in the use of particular olefinic starting material which is decomposed in the course of the alkylation reactions and in the use of other types of catalyst than sulfuric acid. The type of reaction with which the invention is concerned is therefore distinctly novel over the prior art.

In one specific embodiment the present invention comprises the alkylation of aromatic hydrocarbons in the presence of catalysts by olefins formed by the depolymerization of olefins higher in molecular weight than butylenes, the process being essentially one of "depolyalkylation."

According to the present invention any of the aromatic hydrocarbons may be alkylated including benzene and its homologs, members of the naphthalene series and members of the anthracene or higher polynuclear cyclic series, obviously with somewhat modified conditions of operation when alkylating different compounds. The olefins employed are all of higher molecular weight than propylene and preferably consist of compounds of at least 6-carbon atoms to the molecule since the ease of decomposition of the olefins to yield lower molecular weight olefinic residues increases generally with the molecular weight of the olefin. Thus, the butenes, which may be considered as dimers of ethylene require very severe conditions for their depolymerization and the reaction is not selective since large quantities of by-products as well as ethylene are formed and only relatively small yields of ethyl derivatives of aromatics are obtained. Considering hexenes as dimers of propylene, these undergo depolymerization more easily to form propylene molecules which are caused to alkylate aromatic compounds. With increasing molecular weight of the olefins the alkylation reactions become progressively easier to accomplish. Catalysts which may be employed in effecting the type of reactions which characterize the invention may comprise sulfuric acid, phosphoric acid, and anhydrous metal halides such as for example, aluminum chloride, zinc chloride, and ferric chloride. The adaptation of these different alternative compounds will depend upon the compounds undergoing reaction, the temperature and corresponding phase conditions found most suitable and the need for a more active or a less active catalyst.

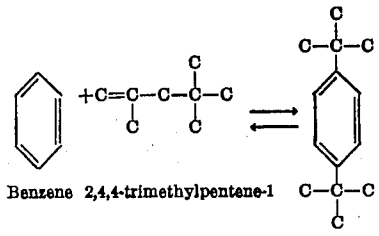
In conducting the process for the alkylation of normally liquid aromatics with normally liquid olefins the simplest procedure is to add a proportioned mixture of the hydrocarbons to a liquid catalyst such as 96% sulfuric acid or 90–100% orthophosphoric acid during vigorous agitation. Such processes may be made continuous by intimately mixing streams of liquid acids and hydrocarbon mixtures and causing the materials to pass through mixing devices which maintain intimate contact for sufficient time to insure completion of the desired reactions. In any event when the reactions are complete as determined by tests, the hydrocarbon layer is separated from the acid layer by either gravitational settling or centrifuging and the hydrocarbon layer fractionated to recover the desired alkyl derivatives.

When employing solid catalysts such as aluminum chloride the suspension of catalyst in the hydrocarbon mixture may be agitated in batch treaters until the reactions have been completed or as before as in the case of liquid catalysts, the mixture may be passed through a tortuous path in some type of baffled mixer to accomplish the same result.

The temperature of treatment of any given aromatic with higher molecular weight olefins to effect their alkylation with the olefin depolymerization products will necessarily vary with the molecular weight of the olefin and the activity of the catalyst and other factors. Pressure may be used when temperatures substantially above atmospheric or approaching the boiling points of the hydrocarbons are employed, functioning principally to prevent loss of material by vaporization. As a rule, however, the temperature ranges are low and are comprised within the approximate range of 0–50° C. so that pressure is seldom necessary.

To illustrate the type of reactions involved in the present process the following equation is given which indicates the reactants and the principal product formed when depolyalkylation is brought about between benzene and the dimers of isobutene which consists principally of 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2.

The equation is given for the first-named compound.



It is evident from the course of the reaction as indicated by the above structural equation that the octene has undergone scission at the bond between the two central carbon atoms to leave two tertiary groups. Since similar products are obtained when di-isobutene produced by the polymerization of isobutene is substituted for the single compound in the above equation, it is evident that the 2-pentene derivative undergoes a similar splitting. In the case of olefins having an odd number of carbon atoms as heptenes or nonenes or higher molecular weight olefinic compounds the reactions will be of a somewhat more complicated nature since the break between the carbon atoms may occur at different points in the aliphatic chain and produce different types of alkylated benzene derivatives. For instance, a heptene may yield substantial quantities of propyl-butyl substituted compounds while a nonene may yield principally propyl derivatives due to its depolymerization into three molecules of propylene.

The following examples are given to indicate results which are typical of the process though they are not given with the intention of unduly limiting the invention's scope.

Example I

A mixture consisting of 140 parts by weight of a mixture of di-isobutenes boiling within the narrow range of 102–104° C. and 97 parts by weight of benzene was added to 180 parts by weight of 96% sulfuric acid, the rate of addition being slow enough to be consistent with the maintenance of substantially atmospheric temperature. After the total hydrocarbon mixture had been added, the agitation was stopped and the acid and hydrocarbon layers allowed to separate.

The hydrocarbon layer after neutralizing with dilute caustic soda was carefully fractionated to produce three fractions as listed below.

Fraction 164–178° C. consisting of about equal parts of mono tertiary butyl benzene and p-ditertiary butyl benzene with a melting point of 78° C.

Fraction 216–250° C. containing a major proportion of the p-ditertiary butyl benzene as in the first fraction.

A fraction boiling at 149–154° C. under a pressure of 9 mm. absolute consisting principally of various tritertiary butyl benzenes as indicated by the analysis of the total fraction given below:

	C	H	Mol. wt.
Calculated for $C_6H_3(C_4H_9)_3$	87.80	12.20	246
Found	87.32	12.38	236

Example II

In this case a mixture of tri-isobutenes and benzene in about the same proportions as in Example I was passed into sulfuric acid in the same manner. The same type of products were obtained as before a somewhat larger proportionate yield of the more highly alkylated compounds.

Example III

23.4 parts by weight of benzene and 29.4 parts by weight of di-n-butene were mixed and added slowly to 105 parts by weight of 96% sulfuric acid. The principal fraction obtained from the hydrocarbon layer boiled between 247 and 251° C. and consisted principally of p-di-sec.-butyl benzene, since it yielded an oxidation principally terephthalic acid as indicated by the melting point of the dimethyl ester which checked the observed value of 140° C. A small yield of tri-sec.-butyl benzene was also obtained.

Example IV

In this case a suspension of 20 parts by weight of anhydrous aluminum chloride in 112 parts by weight of di-isobutene and 100 parts by weight of benzene was agitated for some time at 0° C. while introducing a small but regular stream of hydrogen chloride. After separation of the aluminum chloride sludge from the hydrocarbon layer, it was found that the major portion of the products consisted of mono-ter.-butyl benzene.

The novelty and utility of the process of the present invention are evident from the foregoing specification and the numerical data presented although neither section is intended to be unduly limiting upon the proper scope of the invention.

By the term "depolyalkylation", employed in the appended claims, we mean the herein described reaction wherein an olefin hydrocarbon is split or depolymerized into olefin fragments of lower molecular weight and wherein an aromatic hydrocarbon is alkylated by such olefin fragments.

We claim as our invention:

1. A process for producing alkylated aromatics which comprises subjecting a mixture of an aromatic hydrocarbon and an olefin of higher molecular weight than butylene to depolyalkylation.

2. A process for producing alkylated aromatics which comprises subjecting a mixture of an aromatic hydrocarbon and an olefin of higher molecular weight than butylene to depolyalkylation in the presence of a polymerization catalyst and at a temperature within the approximate range of 0 to 50° C.

3. A process for producing alkylated aromatics which comprises subjecting a mixture of an aromatic hydrocarbon and an olefin of higher molecular weight than butylene to depolyalkylation in the presence of a mineral acid catalyst and at a temperature within the approximate range of 0 to 50° C.

4. A process for producing alkylated aromatics which comprises subjecting a mixture of an aromatic hydrocarbon and an olefin of higher molecular weight than butylene to depolyalkylation in the presence of a metallic halide catalyst and at a temperature within the approximate range of 0 to 50° C.

5. A process for producing alkylated aromatics which comprises subjecting a mixture of an aromatic hydrocarbon and an olefin of higher molecular weight than butylene to depolyalkylation in the presence of aluminum chloride and hydrogen chloride.

6. A process for producing alkylated aromatics which comprises subjecting a mixture of an aromatic hydrocarbon and an olefin of higher molecular weight than butylene to depolyalkylation in the presence of aluminum chloride and hydrogen chloride and at a temperature of approximately 0 to 50° C.

7. A process for producing alkylated aromatics which comprises subjecting a mixture of an aromatic hydrocarbon and a butene polymer to depolyalkylation.

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