This invention relates to the treatment of a mono-nuclear aromatic hydrocarbon with an olefin to produce a high yield of a mono-alkylated mono-nuclear aromatic hydrocarbon. More specifically the invention is concerned with the production of mono-isopropyl benzene in the presence of a particular catalyst and under operating conditions found to give high yields of mono-isopropyl benzene.

Mono-isopropyl benzene is particularly important as a constituent of gasoline boiling range motor fuels of high antiknock value. It is also in considerable demand as an intermediate in the synthesis of higher molecular weight aromatic hydrocarbons such as cymene and other polyalkylated benzene hydrocarbons containing at least one isopropyl group per molecule.

It is recognized that in general the catalytic alkylation of aromatic hydrocarbons has been known for some time. However, the present invention differentiates from the prior art on this subject in the use of particular conditions of operation which have been found necessary in the presence of solid phosphoric acid catalyst in order to obtain high yields of mono-isopropyl benzene with relatively small production of more-highly propylated benzenes.

In one specific embodiment the present invention comprises a process for producing mono-isopropyl benzene by subjecting benzene and propylene to contact with a solid phosphoric acid catalyst at a temperature between about 150° and about 450° C. under a pressure of at least 100 pounds per square inch.

Benzene which is alkylated with propylene according to the process of this invention is obtainable from several sources including the distillation of coal, the dehydrogenation of naphthenic hydrocarbon fractions containing cyclohexane, and the dehydrogenation and cyclization of aliphatic hydrocarbons containing 6 carbon atoms per molecule in straight chain arrangement such as normal hexane and the straight-chain hexanes.

Propylene utilized as alkylation agent in the present instance may be obtained from gases produced in the cracking of petroleum hydrocarbons, by the dehydration of propylene alcohols, and by any other suitable means which result in the formation of either substantially pure propylene or a hydrocarbon fraction containing substantial amounts of this olefinic hydrocarbon. Such fractions containing propylene also generally contain certain amounts of propane when they are derived from gases produced by cracking or dehydrogenation of hydrocarbons.

An essential material utilized in preparation of the preferred solid alkylation catalysts is phosphoric acid which may constitute 80% or more of the catalyst material, and in most cases is over 50% by weight thereof. Of the various acids of phosphorus, ortho- or pyro-phosphoric acids are generally preferred on account of their alkylating abilities, their cheapness, and the readiness with which they may be procured, although the invention is not restricted to their use but may employ catalyst composites formed from any of the other catalytically active acids of phosphorus, particularly those in which phosphorus has a valence of 5, since these are generally more active than those in which phosphorus has a valence of 3. It is not intended to infer, however, that the acids of phosphorus which may be employed will produce identical effects upon the alkylation reaction, as each acid will exercise its own characteristic activity. The alkylating activity of a given catalyst is also dependent upon the ratio of acid to siliceous adsorbent employed in producing the calcined composite catalytic material.

Solid phosphoric acid catalysts, which are particularly utilisable in the present alkylation process, may be made by mixing an acid of phosphorus such as ortho-, pyro-, or tetra-phosphoric acid with a finely divided generally siliceous solid carrier (such as diatomaceous earth, prepared forms of silica, raw and acid-treated clays, etc.) to form a rather wet paste; calcining at temperatures generally below about 500° C. to produce a solid cake; grinding and sizing to produce particles of usable mesh. If the calcination is carried out at temperatures above about 300° C. it is sometimes desirable to rehydrate the catalyst granules at a temperature between about 200° and about 300° C. and preferably at about 260° C. to produce an acid composition corresponding to high alkylation activity. The catalyst preparation procedure may be varied by forming particles of the original paste, by extrusion, or by pelleting methods, after which the formed particles are calcined and, when necessary, rehydrated.

In the reactions taking place during calcination it is evident that some acid is "fixed" on the carrier and it is probable that some metaphosphoric acid, which is not as active under these conditions, is formed. The rehydrated step evidently produces an acid composition corresponding closely to the pyro-acid having a formula H₃P₂O₅. Unless rehydration is practised the temperature of approximately 300° C. should generally not be exceeded in the calcination step.
This description of a solid phosphoric acid catalyst and of its preparation is not exhaustive, as both have been described generally in United States Letters Patent Nos. 1,993,513; 2,120,702; 2,157,208; and others.

Because of the possibility of varying both the amount of phosphoric acid ingredients and the relatively inert adsorbing materials which go to form the solid phosphoric acid catalyst masses, a number of alternative catalysts exist each of which will have its own particular catalyzing potency which will not be exactly equivalent to those of other masses of different compositions.

The different solid phosphoric acid catalysts which may be prepared as herein described, are hygroscopic and accordingly are usually ground, sized or formed, and preserved for use with the avoidance of unnecessary contact with moist air.

In effecting reaction between benzene and propylene according to the process of the present invention, the reacting hydrocarbons are subjected to contact with the solid phosphoric acid catalyst at a temperature preferably from about 150° to about 325° C. although alkylation will proceed slightly at a temperature of about 100° C. Temperatures higher than those mentioned hereabove but generally not in excess of about 450° C. are sometimes utilized but when excessive temperatures are employed there is generally a relatively rapid loss in activity of the catalyst probably due in part to loss of water therefrom and also to the accumulation thereon of carbonaceous and hydrocarbonaceous deposits. It is preferable that the reaction mixture be maintained under a pressure generally of from about 100 to about 1000 pounds per square inch or more. While lower pressures as low as atmospheric are operable to a limited degree, such low pressures are undesirable since under these conditions more polyisopropyl benzenes are formed and the catalyst life is shorter than when the pressure is sufficient to keep in liquid state some of the benzene and/or propylated benzenes. Pressures higher than about 1000 pounds per square inch are usually necessary. In order that the catalyst may retain its alkylation activity for a relatively long period of time it is preferable that the operating pressure be sufficient to maintain in liquid state a substantial proportion of the benzene or at least of the isopropyl benzene resulting from interaction of propylene with benzene.

Intimate contact of the benzene and propylene with the catalyst may be effected by continuously directing these materials through a reactor containing a stationary bed of granular or otherwise formed solid phosphoric acid catalyst whereby mono-isopropyl benzene and relatively small amounts of more-highly propylated benzenes are formed.

The hydrocarbon mixture subjected to alkylation preferably contains from about 2 to about 20 or more molecular proportions of benzene per 1 molecular proportion of propylene so that formation of mono-isopropyl benzene is the principal reaction of the process. Under these conditions there is only a relatively small formation of more-highly alkylated benzenes and polymer formation is also low or substantially absent. The product from such alkylation reaction is fractionated into mono-isopropyl benzene, more-highly propylated benzenes, and unconverted benzene, the latter being recycled to the alkylation.

Benzene and a hydrocarbon fraction containing substantial amounts of propylene as a 5-pane-propylene fraction may be commingled and passed through a reactor containing a solid phosphoric acid catalyst, or the benzene may be charged to such a reactor while the propylene-containing fraction or a mixture of benzene and propylene is introduced at various points between the inlet and the outlet of the alkylation reactor in such a way that the reaction mixture being contacted with the catalyst will contain a high molecular proportion of benzene relative to propylene throughout the entire reaction and thus favor the formation of mono-isopropyl benzene rather than poly-isopropyl benzene.

Continuous alkylation treatment other than that referred to above may also be carried out in the presence of powdered catalyst in other types of apparatus designed for contacting hydrocarbons with finely divided solid catalyst.

While the method of passing benzene and propylene, either together or countercurrently, through a suitable reactor containing a stationary bed of solid catalyst particles is generally customary procedure, the interaction of these hydrocarbons may also be effected in batch type operation in a closed vessel in which some of the components are preferably in liquid phase and in which the catalyst, generally in finely divided form, is maintained in dispersion or suspension by some method of agitation.

Calcined composites of an acid of phosphorus and a siliceous adsorbent are preferred catalysts for use in the production of mono-isopropyl benzene as they permit continuous reaction of benzene with propylene in the presence of a stationary or fixed bed catalyst and thus make it possible to substantially avoid over-alkylation to poly-isopropyl benzenes as well as to simplify certain mechanical problems, and to avoid corrosion difficulties encountered when this reaction is carried out in the presence of a liquid phosphoric acid. Further, the solid phosphoric acid catalysts herein described have the advantages over aluminum chloride utilized for the same purpose that said benzene form substantially no stable addition compounds with complexes with or complexes with and/or olefinic hydrocarbons as is characteristic of catalysts containing aluminum chloride. Also the product obtained in the presence of solid phosphoric acid catalyst is usually immediately ready for distillation and does not need to be washed or otherwise treated to remove any as is the case when aluminum chloride is the alkylation catalyst utilized.

While the alkylation reaction of the present process is not understood completely, it results in the combination of benzene with propylene to produce isopropyl benzene, which in turn can undergo further reaction with one or several molecular proportions of propylene to produce di- and poly-isopropyl benzenes. Within certain limits it is possible to produce mainly mono-isopropyl benzene by proper adjustment of catalyst activity, ratio of benzene to propylene, and such operating conditions as temperature, pressure, rate of feed of the reacting hydrocarbons, etc. In general, when the operating temperature is relatively high, the rate of feed is greater than that utilized in the lower reaction temperatures. Also higher pressures are generally preferred when utilizing the higher catalyst temperatures as increased superatmospheric pressure aids in keeping in liquid state a certain amount of the benzene or propylated benzenes, the latter formed in the alkylation reaction. We believe that such
A mixture of 3.8 molecular proportions of benzene and 1 molecular proportion of propylene was passed through a steel reactor containing a solid phosphoric acid catalyst formed previously by calcining a composite of pyrophosphoric and diphosphoric acid and distameric earth. In this run the catalyst temperature was 280° C., the operating pressure was 100 pounds per square inch, and 1 volume of benzene was charged per hour through one volume of reactor space containing the catalyst as a filling material. Of the propylene charged, 50% reacted per pass and the alkylation product was formed containing 76 mole per cent of mono-isopropyl benzene and 24 mole per cent of a poly-isopropyl benzene mixture. The unconverted propylene recovered from the alkylation product was suitable for recycling to the alkylation reaction.

Example III

A mixture of 8 molecular proportions of benzene and 1 molecular proportion of propylene was passed continuously through a steel reactor containing solid phosphoric acid catalyst maintained at the temperatures and pressures shown in the following table. In each of the three runs upon which data are herein given, the mixture of benzene and propylene was charged at an hourly liquid space velocity of 3.0, that is, 3.0 volumes of liquid was charged per hour per volume of reactor space containing the catalyst layer. In each of the runs, substantially all of the propylene reacted forming mono-isopropyl benzene and poly-isopropyl benzenes with substantially no polymer formation. The pressures employed in the runs indicated in the table were sufficient to maintain in liquid state a substantial proportion of the benzene and propylated benzene.

Table

<table>
<thead>
<tr>
<th>(Alkylation of benzene with propylene)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run No.</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>Catalyst temperature, °C.</td>
</tr>
<tr>
<td>Pressure, pounds per square inch</td>
</tr>
<tr>
<td>Length of run, hours</td>
</tr>
<tr>
<td>Reaction product, weight per cent of:</td>
</tr>
<tr>
<td>Mono-isopropyl benzene</td>
</tr>
<tr>
<td>Poly-isopropyl benzene</td>
</tr>
<tr>
<td>Ratio of mono-isopropyl to poly-isopropyl benzene formed</td>
</tr>
<tr>
<td>Mono-isopropyl benzene yield, percent by weight of total alkylated benzene</td>
</tr>
<tr>
<td>Rate of production of isopropyl benzene, pounds per hour per pound of catalyst</td>
</tr>
<tr>
<td>Poly</td>
</tr>
</tbody>
</table>

Example I

A mixture of 3.8 molecular proportions of benzene and 1 molecular proportion of propylene was passed through a steel reactor containing a solid phosphoric acid catalyst formed previously by calcining a composite of pyrophosphoric and diphosphoric acid and distameric earth. In this run the catalyst temperature was 280° C., the operating pressure was 100 pounds per square inch, and 1 volume of benzene was charged per hour through one volume of reactor space containing the catalyst as a filling material. Of the propylene charged, 50% reacted per pass and the alkylation product was formed containing 76 mole per cent of mono-isopropyl benzene and 24 mole per cent of a poly-isopropyl benzene mixture. The unconverted propylene recovered from the alkylation product was suitable for recycling to the alkylation reaction.

In general the products of the interaction of propylene with a molecular excess of benzene are separated from the unreacted benzene by suitable means such as distillation, and the unreacted portion of the benzene originally charged is returned to the process and mixed with additional quantities of fresh benzene and propylene or propylene-propylene fraction. The total alkylation product thus freed from the excess of originally charged benzene is separated into isopropyl benzene and more-highly alkylated benzenes by distillation at ordinary pressure or at a reduced pressure, or by other suitable means. Sometimes a poly-isopropyl benzene fraction is returned to the process and mixed with the benzene and propylene being directed to contact with the catalyst.

A benefit of this is to wash the catalyst and remove hydrocarbonaceous deposits which tend to cut down catalytic activity. A further benefit may be to increase the ratio of mono-isopropyl benzene formed over the polypropyl benzene formed. In case propylene reacts incompletely with benzene as may occur when the charging rates of benzene and propylene are too high, the unreacted with a molecular excess of benzene is washed in the condenser or other suitable means and recycled to the process.

When the alkylation is carried out at a temperature above about 200° to 250° C., it is sometimes advantageous to add to the alkylation mixture a small amount of an aqueous fluid in order to offset deterioration of the catalyst due to dehydrogenation. Generally not more than about 5%, but preferably from about 0.1 to about 2% by weight of an aqueous fluid such as water or steam is used for the purpose of preserving catalyst activity. Alternatively, small amounts of propylene or isopropyl alcohol may be charged with the benzene and propylene to provide the desired quantity of water needed to prevent undue dehydrogenation of the catalyst. This use of a propylene alcohol is generally possible at temperatures above about 250° C. because of the fact that under the operating conditions the propyl or isopropyl alcohol undergoes a certain amount of dehydrogenation into propylene and water, the former being utilizable in the alkylation reaction while the latter aids in prolonging the active life of the catalyst.

The following examples illustrate the character of results obtained in specific embodiments of the present process, although the examples given are not introduced with the intention of unduly restricting the generally broad scope of the invention.
The catalysts used in the runs referred to above were still active and could have been employed for longer periods of time. These runs, in which the benzene to propylene ratio in the charge was 8:1 and the pressure was sufficient to provide a liquid wash for the catalyst, yielded alkylation products containing 95% by weight or more of mono-isopropyl benzene and not more than 5% of more-highly alkylated benzenes.

The above examples show that in order for at least 75% by weight of the benzene alkylation product to consist of mono-isopropyl benzene it is necessary that more than 3 molecular proportions of benzene be present throughout the entire reaction per molecular proportion of propylene charged. With benzene to propylene ratios of about 5:1 and higher, the alkylation product contains 90% or more of mono-isopropyl benzene. An operating pressure of at least 100 pounds per square inch is also necessary not only for insuring long life of the catalyst but also because of the fact that higher yields of mono-isopropyl benzene relative to poly-isopropyl benzenes result when the operating pressure is sufficient to provide a liquid wash for the catalyst. Catalyst temperatures of from about 150° to about 225° C. are preferred for use in the alkylation of benzene to high yields of mono-isopropyl benzene.

The novelty and utility of the process of the present invention are evident from the preceding specification and examples given, although neither section is intended to unduly limit its generally broad scope.

We claim as our invention:

1. A process for producing mono-isopropyl benzene which comprises subjecting benzene and propylene in molar proportion greater than 3:1 to contact with a solid phosphoric acid catalyst under alkylation conditions of temperature between about 150° and about 325° C. and pressure of at least 100 pounds per square inch such that formation of mono-isopropyl benzene is the principal reaction of the process.

2. A process for alkylation benzene with propylene in the presence of solid phosphoric acid catalyst which comprises contacting the benzene and propylene in molar proportions greater than 3:1 with the catalyst under conditions of a temperature between about 150° and about 450° C. and pressure of at least 100 pounds per square inch, such that the formation of mono-isopropyl benzene constitutes the principal reaction.

3. A process for alkylation benzene with propylene in the presence of solid phosphoric acid catalyst which comprises contacting the benzene and propylene in molar proportions of more than 5:1 with the catalyst under conditions of temperature between about 150° and about 450° C. and pressure of at least 100 pounds per square inch, such that the alkylated benzenes formed comprise at least 90% of mono-isopropyl benzene.

4. In a process for alkylation benzene with propylene in the presence of solid phosphoric acid catalyst under such conditions that alkylation of benzene is the principal reaction in the process, the improvement which comprises contacting the benzene and propylene in molar proportion greater than 3:1 with the catalyst at a temperature between about 150° and about 325° C. under a sufficiently elevated pressure above 100 pounds per square inch to maintain in the liquid state at least a portion of the hydrocarbons present.