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PREPARATION OF ALKYLBENZENES

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This invention relates to the preparation of alkylbenzenes and in particular it concerns the preparation of 1,2,3-trialkylbenzenes and 1,2,3,4-tetraalkylbenzenes.

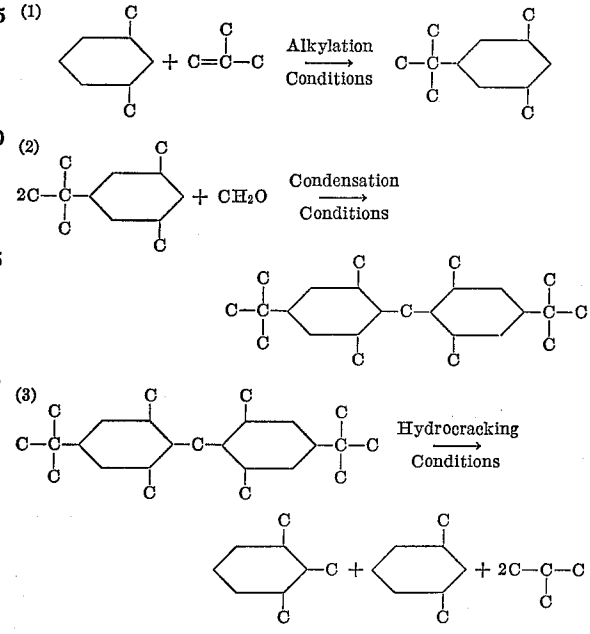
When benzene or alkylbenzenes are alkylated, a variety of isomeric polyalkylbenzenes is produced. Of the polyalkylbenzenes produced, the predominant isomer is usually the more symmetrical polyalkylbenzene, e.g., 1,3,5-trialkylbenzene, 1,2,4,5-tetraalkylbenzene. Vicinally substituted polyalkylbenzenes, e.g., 1,2,3-dialkylbenzenes are not produced, except in very minor quantities, by conventional alkylation techniques. Since these vicinally substituted polyalkylbenzenes are desired feed stocks for conversion to chemicals, a process capable of producing these isomers as the predominant product is needed.

An object of this invention is to provide a process which is selective for the production of vicinally substituted polyalkylbenzenes such as 1,2,3-trialkylbenzenes and 1,2,3,4-tetraalkylbenzenes in preference to the other polyalkylbenzene isomers. Another object is to provide a process for converting 1,2- and 1,3-dialkylbenzenes to 1,2,3-trialkylbenzenes, and for converting 1,2,4-trialkylbenzenes to 1,2,3,4-tetraalkylbenzenes. A further object is to provide a process for producing vicinally substituted polyalkylbenzenes whose alkyl substituents have less than 4 carbon atoms. Other objects and advantages of the invention will be apparent from the detailed description thereof.

In accordance with the present invention, 1,2,3-trialkylbenzenes are prepared by steps of (1) alkylating 1,2- or 1,3-dialkylbenzenes and introducing a tertiary alkyl substituent into the benzene ring, (2) condensing the monoalkylated polyalkylbenzene with an aldehyde which has from 1 to 3 carbon atoms per molecule and thereby producing an alkyl-substituted diarylalkane, and (3) cracking the diarylalkane to remove the tertiary alkyl substituents and splitting the diarylalkane into two polyalkylbenzene molecules. One of the polyalkylbenzene molecules produced is identical with the polyalkylbenzene employed as feed and the other polyalkylbenzene molecule has one more alkyl substituent than was contained in the feed polyalkylbenzene. This additional alkyl substituent is attached to the benzene ring adjacent the other alkyl substituents so as to form 1,2,3-trialkylbenzene from the 1,2- and 1,3-dialkylbenzene employed as feed. In the same fashion, 1,2,3,4-tetraalkylbenzenes are produced from 1,2,4-trialkylbenzenes. The vicinally substituted polyalkylbenzenes produced by this process are those which have less than 4 carbon atoms per alkyl substituent, and in preparing these components, the alkyl substituents of the feedstocks also will contain less than 4 carbon atoms per alkyl substituent. The invention is very suitable for preparing those polyalkylbenzenes whose alkyl substituents are no longer than 2 carbon atoms in length, and especially useful when the alkyl substituent is a methyl grouping. The process is preferably carried out using as feedstocks polyalkylbenzenes all of whose alkyl substituents have the same carbon atoms and using an aldehyde which has the same number of carbon atoms per molecule as is contained in the alkyl substituent. The

cracking step is carried out under conditions which effect no substantial isomerization of the alkyl substituents around the benzene ring. By carrying out the cracking of the diarylalkane in the presence of a hydrogen, usually using at least 1 mol of hydrogen per mol of diarylalkane and employing a hydrocracking catalyst, the formation of alkylbenzenes which have unsaturated alkyl substituents is avoided. If no hydrogen is employed in the cracking step, alkenyl polyalkylbenzenes can be produced.

The reactions involved in the steps of this invention are graphically illustrated below, wherein 1,3-dimethylbenzene (m-xylene) feedstock is ultimately converted to 1,2,3-trimethylbenzene (hemimellitene).



While Reaction 1 uses 1,3-dimethylbenzene as the feedstock, other 1,3- and 1,2-dialkylbenzenes can be employed. 1,2,4-trialkylbenzenes can be used in the production of 1,2,3,4-tetraalkylbenzenes. Because longer chain length alkyl substituents will be detached during the cracking step, the number of carbon atoms per alkyl substituent attached to the benzene ring of the feedstock should be less than 4 carbon atoms and is suitably one or two carbon atoms in length. To facilitate the production and recovery of a relatively pure product, all of the alkyl substituents attached to the benzene ring preferably should have the same number of carbon atoms per alkyl substituent. To avoid a complicated product recovery system only one polyalkylbenzene compound, rather than a mixture of such compounds, should be employed as the feedstock. Examples of suitable feedstocks are 1,2- and 1,3-dimethylbenzenes, 1,2- and 1,3-diethylbenzenes, 1,2,4-trimethylbenzene, and 1,2,4-triethylbenzene.

The feed polyalkylbenzene is contacted with an alkylating agent which has a tertiary carbon atom in order to introduce a tertiary alkyl grouping into the benzene ring. The alkylating agent is preferably an olefin or a cycloclefin having a tertiary carbon atom, such as isobutylene, diisobutylene, trimethyl ethylene, 1-methylcyclohexene-1 etc. Other alkylating materials such as alkyl halides, preferably alkyl chlorides or alkyl fluorides, secondary or tertiary alcohols, e.g. tertiary butyl alcohol, may also be employed if desired. Since the alkylating agent must have at least one tertiary carbon atom, it therefore has at least 4 carbon atoms per molecule. Alkylating agents containing 8 or less carbon atoms per molecule are preferred.

The catalyst and reaction conditions which may be used in effecting alkylation of the polyalkylbenzene are the conventional catalysts and conditions which are well known in the prior art. Strong acid catalysts such as sulfonic acids, phosphoric acid which is preferably deposited on a solid carrier, hydrogen fluoride, Friedel-Crafts halides such as aluminum chloride, aluminum bromide etc., may be employed. For example the polyalkylbenzene may be alkylated with isobutylene using hydrogen fluoride at a temperature of from about —20° C. to about 75° C. Commercial anhydrous hydrogen fluoride can be used. A wide range of pressures e.g. atmospheric to 1000 p.s.i.g. can be used, the pressure preferably being sufficient to maintain the reaction mixture in the liquid phase. The ratio of olefin to polyalkylbenzene is not critical. It may range from 0.5 to 5 mols of olefin per mol of aromatic. Usually about an equimolar ratio is preferred. Lesser quantities achieve incomplete alkylation and greater quantities achieve some undesired dialkylation if a 1,2-dialkylbenzene is employed as the feedstock. Very little dialkylation occurs when the other polyalkylbenzenes are employed as feedstocks.

The mono-alkylation product, after separation of the catalyst and reactants therefrom, is then condensed with an aldehyde to form a diarylalkane in the manner illustrated by Reaction 2. If polyalkylation products are present in the reaction products from Reaction 1 they can be removed by fractionation. The alkylation products ordinarily need not be neutralized and washed with water to remove any catalyst contained therein since an acid catalyst is employed in Reaction 2. However, if a different catalyst is employed in Reaction 2, removal of any catalyst contained in the alkylated polyalkylbenzene can be effected prior to carrying out Reaction 2. In the condensation step of Reaction 2 the polyalkylbenzene containing one tertiary alkyl substituent is condensed with an aldehyde having from one to three carbon atoms per molecule. The vicinally substituted polyalkylbenzene which is produced by this invention will have as the introduced alkyl grouping, an alkyl substituent which has the same number of carbon atoms as the aldehyde employed in the condensation step. Thus if a vicinally substituted polyalkylbenzene product is desired which has alkyl substituents all having the same number of carbon atoms, each of the alkyl substituents in the feed polyalkylbenzene employed for Reaction 1 should have the same number of carbon atoms and the aldehyde used in Reaction 2 should have the same number of carbon atoms as is contained in the alkyl substituent. Formaldehyde or acetaldehyde, in any of their physical forms, are preferably employed. The aldehyde forms which contain a substantial quantity of water, e.g. formalin, are not preferred since they reduce the condensation reaction rate and increase the tendency of the condensation products toward emulsification. Any of a wide variety of acid condensation catalyst such as aryl sulfonic acids e.g. benzene sulfonic acid, toluene sulfonic acid, low molecular weight alkane sulfonic acids, 90 percent sulfuric acid, boron trifluoride, zinc chloride or the like can be employed. Toluene sulfonic acid is preferred. While the amount of acid condensation catalyst used will vary depending upon the particular catalyst and the conditions employed, it may satisfactorily be used in an amount between 0.1 and 5 parts per part by weight of aldehyde.

The reactants in the condensation step are preferably employed in a ratio of about two mols of mono-alkylated polyalkylbenzene per mol of aldehyde. Molar ratios of between 1:1 and 10:1 can ordinarily be used. When using 80 percent toluene sulfonic acid as the condensation catalyst, molar ratios of mono-alkylated polyalkylbenzene to aldehyde of 2:1 to 5:1 are satisfactory. Between 0.5 and 3 parts of the acid per part by weight of aldehyde may be used. With this catalyst a temperature of from 50° C. to 175° C., suitably the refluxing temperature, and a reaction time of from 0.5 to 10 hours e.g. 2 to 4 hours, is satisfactory. In Reaction 2, a 1,1'-diarylalkane is produced along with minor amounts of higher molecular weight condensation products which are preferably removed by fractionation. In a typical operation the bulk of the hydrocarbon reaction products from the condensation step is separated from the bulk of the catalyst. The hydrocarbons can then be fractionated to recover the diarylalkane. The diarylalkane, preferably diluted with an aromatic such as benzene to prevent it from solidifying, is then preferably processed to remove any catalyst contained therein by techniques such as neutralization followed by water washing, filtering through a suitable solid absorbent such as Attapulgus clay etc., before introducing the diarylalkane into the cracking step.

In the cracking step the diarylalkane is subjected to cracking conditions which split off the tertiary alkyl substituent (which had been introduced into the molecule by Reaction 1 and cleave the bond linking the two benzene rings. The cracking reaction is carried out under conditions whereby no substantial isomerization of the alkyl substituents around the benzene ring is effected. In this manner, one polyalkylbenzene molecule is produced which is identical with the feed polyalkylbenzene employed in Reaction 1 and which can be recycled thereto, and another polyalkylbenzene molecule is produced which is the ultimate product desired i.e. the vicinally substituted polyalkylbenzene which has an additional alkyl substituent having the same number of carbon atoms as were contained in the aldehyde employed in Reaction 2. Thus when 1,2-dialkylbenzene or 1,3-dialkylbenzene is employed as the feed polyalkylbenzene to Reaction 1, the products from cracking will consist of 1,2,3-trialkylbenzene and 1,2-dialkylbenzene or 1,3-dialkylbenzene respectively. If 1,2,4-trialkylbenzene is employed as the feed polyalkylbenzene to Reaction 1, the products of cracking will consist of 1,2,3,4-tetraalkylbenzene and 1,2,4-trialkylbenzene.

The cracking step can be carried out in the presence or absence of hydrogen. If the cracking step is carried out in the absence of hydrogen, then the vicinally substituted polyalkylbenzene produced which has the additional alkyl substituent will contain this additional substituent as an unsaturated alkyl grouping if the aldehyde used contained 2 or 3 carbon atoms. For example if acetaldehyde were condensed with 1,3-dimethyl 5-tertiary butyl benzene and the diarylethane formed were cracked in the absence of hydrogen, then each molecule of the diarylethane would produce a molecule of 1,3-dimethylbenzene and a molecule of 1,3-dimethyl 2-ethenylbenzene. If the cracking is carried out in the presence of hydrogen, saturation of the rupturing carbon to carbon linkages occurs and thus 1,3-dimethyl 2-ethylbenzene is formed.

While the cracking step can be carried out in the presence or absence of a catalyst, a cracking catalyst is preferably employed. In order to effect cracking under conditions which effect no substantial, i.e. less than about 20 percent, isomerization of the alkyl substituents around the benzene ring, a catalyst which is inactive for isomerization should be used. Suitable catalysts are hydrocracking or hydrogenation catalysts such as molybdena-alumina, cobalt molybdate-alumina, platinum-alumina, titania either unsupported or supported on alumina, nickel oxide or nickel sulfide either unsupported or supported, and nickel tungsten sulfide. Silica imparts undesirable isomerization properties to the catalyst and its presence in the catalyst should be avoided. A substantially silica-free catalyst should be used. It is preferred to carry out the cracking step in the presence of hydrogen, i.e. hydrocracking, since the reaction is cleaner, less coke is formed, etc. Suitable cracking conditions comprising a temperature of 350 to 650° C., between about 400 and 500° C. being very satisfactory, and a space velocity of

about 0.5 to about 10 liquid volumes of diarylalkane per volume of catalyst per hour may be used. Pressures of atmospheric to 1500 p.s.i.g. can be employed. When a hydrocracking operation is used, at least about one mol of hydrogen per mol of diarylalkane is introduced into the cracking zone. It is preferred to use more than this minimum amount of hydrogen, suitably about 3 to 10 mols of hydrogen per mol of diarylalkane. Also when the hydrocracking technique is used, it is preferred to employ pressures of from 100 to 500 p.s.i.g. As an illustration, di-(2,6-dimethyl 4-tertiarybutylphenyl) methane, which is preferably diluted with an aromatic diluent such as benzene, is contacted with a molybdena-alumina catalyst (containing about 9 weight percent MoO_3) at a temperature of about 500° C. and a pressure of about 100 p.s.i.g. while employing 4 mols of hydrogen per mol of diarylmethane and 1.0 L.H.S.V. The products from the hydrocracking step are recovered after the completion of the reaction and the vicinally substituted alkylbenzenes (1,2,3-trimethylbenzene) are separated by the usual fractionation techniques.

In a particular embodiment of the invention a mixed C_8 aromatic fraction such as might be obtained by the solvent extraction of a reformate fraction containing C_8 aromatics which include the isomeric xylenes and ethylbenzene, can be employed as the feedstock in this invention. In Reaction 1 the meta-xylene, ortho-xylene, and ethylbenzene are alkylated and the para-xylene is essentially non-alkylated. This latter compound can then be recovered from the alkylation products. Any dialkylation products which are produced (they will be formed primarily from ethylbenzene) can be separated by fractionation. The monoalkylated alkylbenzenes are then condensed with formaldehyde to form the corresponding diarylmethanes which are subsequently hydrocracked. The products from hydrocracking are fractionated to remove toluene and other lower boiling hydrocarbons overhead. A xylene fraction is next recovered which can be recycled to the alkylation step. A bottoms fraction consisting of uncracked diarylmethane, which can be recycled to the hydrocracking step, is separated from an overhead stream consisting of 1,2,3-trimethylbenzene and ethyltoluenes. Since the ethyltoluenes boil at temperatures which are about 10 to 15° C. lower than the 1,2,3-trimethylbenzene, the latter can be recovered in purified form by precise fractionation.

As an illustration of the process of this invention, hemimellitene (1,2,3-trimethylbenzene) was produced from an initial feedstock of m-xylene (1,3-dimethylbenzene). In the first step m-xylene was alkylated with diisobutylene. The alkylation reaction was carried out by contacting m-xylene with about 2 mols of diisobutylene per mol of m-xylene at about 100° C. for several hours. Commercial anhydrous toluene sulfonic acid catalyst was employed as the catalyst. The mono-alkylated product, i.e. tertiary butylxylene, was recovered from the alkylation products and was then condensed with formaldehyde to form the diarylmethane. The condensation reaction was carried out by refluxing tertiary butylxylene with paraformaldehyde (2:1 molar ratio of aromatic to aldehyde) and commercial anhydrous toluene sulfonic acid (amount of acid equal in weight to the amount of aldehyde) for about 4 hours. The products of condensation were diluted with about 2 parts of benzene. The hydrocarbon layer containing the diarylmethane was then decanted from the acid layer. The decanted hydrocarbons were then passed through a layer of Attapulgus clay and a layer of silica gel. Thereafter they were hydrocracked. The hydrocracking step was effected by contacting an 18 percent solution of the diarylmethane in benzene with a molybdena-alumina catalyst (9 percent MoO_3) at a temperature of 450° C. and at atmospheric pressure while employing a hydrogen to diarylmethane molar ratio of about 6:1 and a space velocity of about 1 liquid volume of hydrocarbon/volume of catalyst/hour. An infrared analysis of the products from hydrocracking was made. It was found that 89 percent of the trimethylbenzene fraction consisted of 1,2,3-trimethylbenzene, the remainder being 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene.

A similar experiment was carried out in which meta-xylene was alkylated with propylene, the mono-alkylate was then condensed with formaldehyde, and the resulting diarylmethane was hydrocracked. In this experiment only 42 percent of the trimethylbenzene fraction consisted of 1,2,3-trimethylbenzene. In another experiment wherein 1,2,4-trimethylbenzene was alkylated with propylene, the mono-alkylated product condensed with formaldehyde, and the resulting diarylmethane hydrocracked, the tetramethylbenzene fraction consisted of 60 percent 1,2,3,4-tetramethylbenzene. These experiments illustrate the importance of using tertiary olefins rather than propylene, ethylene, etc. In view of the much greater selectivity for producing the vicinally substituted polyalkylbenzene when isobutylene rather than propylene was employed as the alkylating agent, it would be expected that if isobutylene rather than butylene were employed in alkylating 1,2,4-trimethylbenzene, the tetramethylbenzene fraction produced on hydrocracking would consist of more than 90 percent of 1,2,3,4-tetramethylbenzene. In otherwise comparative experiments, except that Reaction 1 was omitted i.e. 1,3-dimethylbenzene was not alkylated with a tertiary olefin, the trimethylbenzene fraction produced upon hydrocracking contained only 4 percent 1,2,3-trimethylbenzene and 87 percent 1,2,4-trimethylbenzene. This emphatically shows interdependence of the three steps of this process and the criticality of employing these steps in combination to produce the vicinally substituted polyalkylbenzenes.

Thus having described the invention what is claimed is:

1. A process for preparing 1,2,3-trialkylbenzenes and 1,2,3,4-tetraalkylbenzenes whose alkyl substituents contain less than 4 carbon atoms per substituent which process comprises alkylating at least one polyalkylbenzene feedstock selected from the group consisting of 1,2-dialkylbenzenes, 1,3-dialkylbenzenes and 1,2,4-trialkylbenzenes whose alkyl substituents contain less than 4 carbon atoms per substituent with an alkylating agent having at least one tertiary carbon atom per molecule and thereby forming a mono-tertiary alkyl-substituted polyalkylbenzene, condensing the mono-alkylated polyalkylbenzene with an aldehyde containing from 1 to 3 carbon atoms per molecule and forming an alkyl-substituted diarylalkane, subjecting the diarylalkane to cracking conditions which effect no substantial isomerization of the alkyl substituents whereby the tertiary alkyl substituents are removed and the diarylalkane is split into two polyalkylbenzene molecules, one of which molecules is identical with the feed polyalkylbenzene and the other polyalkylbenzene molecule having one more alkyl substituent than was contained in the feed polyalkylbenzene and which additional substituent has the same number of carbon atom as the aldehyde, and thereby forming 1,2,3-trialkylbenzenes from 1,2- and 1,3-dialkylbenzenes and forming 1,2,3,4-tetraalkylbenzenes from 1,2,4-trialkylbenzenes.

2. The process of claim 1 wherein each of the alkyl substituents attached to the benzene ring have the same number of carbon atoms and wherein the aldehyde has the same number of carbon atoms per molecule as the alkyl substituents.

3. The process of claim 1 wherein each alkyl substituent has two carbon atoms and wherein the aldehyde has two carbon atoms.

4. The process of claim 1 wherein the cracking step is carried out under hydrocracking conditions comprising the use of a hydrocracking catalyst and at least one mol of hydrogen per mol of diarylalkane.

5. A process for preparing 1,2,3-trimethylbenzenes and 1,2,3,4-tetramethylbenzenes which comprises alkylating

at least one polymethylbenzene feedstock selected from the group consisting of 1,2-dimethylbenzene, 1,3-dimethylbenzene and 1,2,4-trimethylbenzene with an alkylating agent having at least one tertiary carbon atom per molecule and thereby forming a mono-tertiary alkyl-substituted polymethylbenzene, condensing the mono-alkylated polymethylbenzene with an aldehyde having one carbon atom per molecule and forming an alkyl-substituted diarylmethane, hydrocracking the diarylmethane in the presence of at least one mole of hydrogen per mol of diarylmethane and a hydrocracking catalyst which effects no substantial isomerization of the alkyl substituents and whereby tertiary alkyl substituents are removed from the diarylmethane and the diarylmethane is split into two polymethylbenzene molecules, one of which molecules is identical with the feed polymethylbenzene and the other polymethylbenzene molecule having one more methyl substituent than was contained in the feed polymethylbenzene, the additional methyl substituent being attached to that position in the benzene ring by virtue of the alkylation, condensation and hydrocracking steps so that 1,2- and 1,3-dimethylbenzenes are converted to a trimethylbenzene product containing a predominant amount of 1,2,3-trimethylbenzene and the 1,2,4-trimethylbenzene is converted to a tetramethylbenzene product containing a predominant amount of 1,2,3,4-tetramethylbenzene.

6. The process of claim 5 wherein the feedstock is 1,2-dimethylbenzene and wherein the trimethylbenzene product contains a predominant amount of 1,2,3-trimethylbenzene.

7. The process of claim 5 wherein the feedstock is 1,3-dimethylbenzene and wherein the trimethylbenzene product contains a predominant amount of 1,2,3-trimethylbenzene.

8. The process of claim 7 wherein the feedstock is a mixture of C_8 aromatic isomers.

9. The process of claim 5 wherein the feedstock is 1,2,4-trimethylbenzene and wherein the tetramethylbenzene product contains a predominant amount of 1,2,3,4-tetramethylbenzene.

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