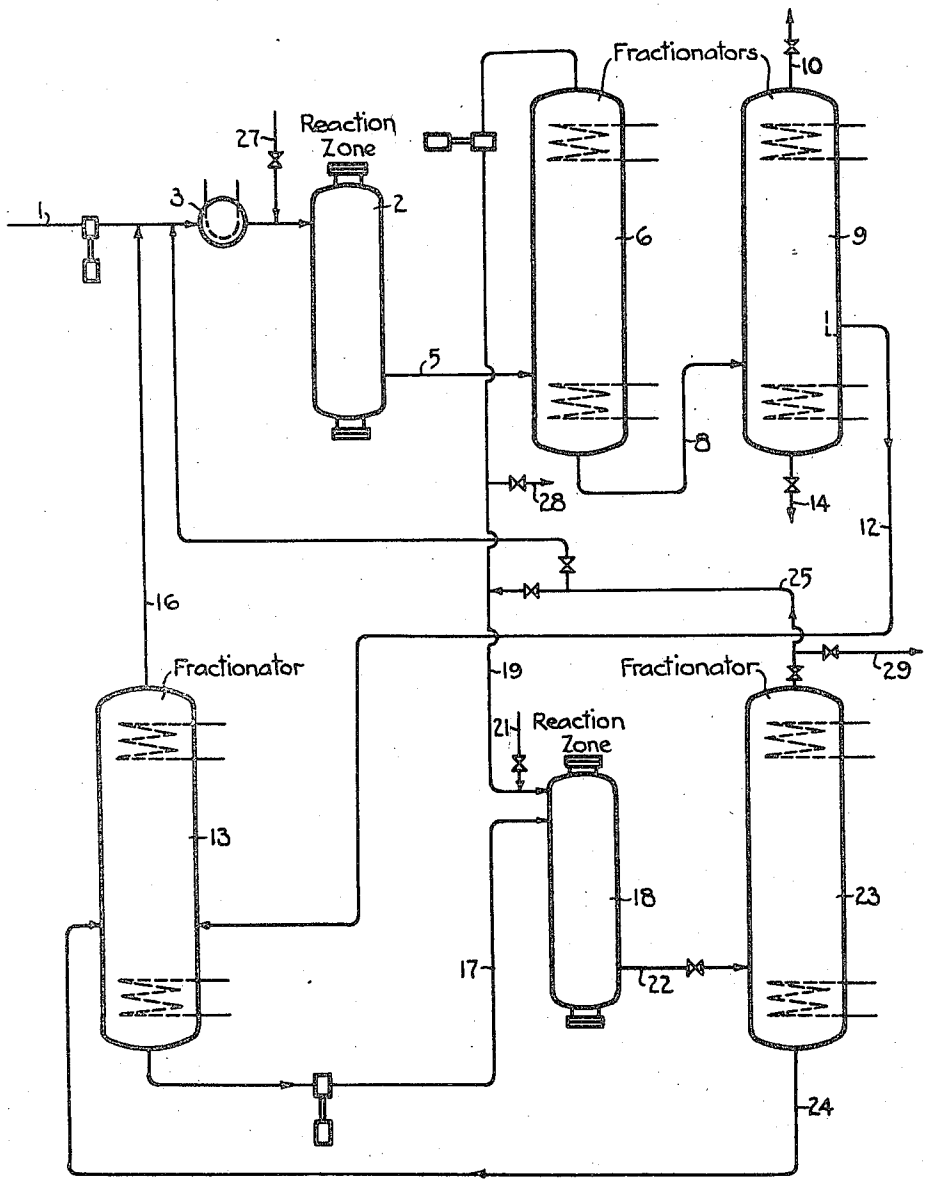
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CONVERSION OF ALKYL AROMATIC HYDROCARBONS INTO ALKENYL AROMATIC HYDROCARBONS

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CONVERSION OF ALKYL AROMATIC HYDROCARBONS INTO ALKENYL AROMATIC HYDROCARBONS

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The present invention relates to the production of olefin-substituted aromatic hydrocarbons from alkyl aromatic hydrocarbons containing at least one alkyl group of at least three carbon atoms. The invention relates more particularly to the production of vinyl aromatic hydrocarbons from alkyl aromatic hydrocarbons containing at least one substituent isopropyl group. A specific embodiment of the invention relates to the production of styrene from isopropyl benzene.

The olefin-substituted aromatic hydrocarbons are employed as starting or intermediate materials in a great number of important fields of application. The vinyl aromatic hydrocarbons, for example, are of value as starting materials in the production of synthetic rubber and a wide variety of chemical derivatives. The alkyl aromatic hydrocarbons constitute an important potential source of olefin-substituted aromatics. Thus a straightforward dehydrogenation of an alkyl aromatic provides the corresponding olefin-substituted aromatic hydrocarbon. Such processes are, however, dependent upon the alkyl aromatic corresponding to the desired olefin-substituted aromatic as charge. These processes therefore exclude the use of alkyl aromatics often more readily available or produced more economically than the alkyl aromatic corresponding to the olefin-substituted aromatic required. They are rendered particularly unattractive where the alkyl aromatic corresponding to the olefin-substituted aromatic is itself in greater demand than the latter. This is often the case, for example, with hydrocarbons such as ethyl benzene and styrene. The demand for ethyl benzenes as such occasions a need for a source of styrene other than this alkyl aromatic.

Processes have been disclosed heretofore for the production of olefin-substituted aromatics from alkyl aromatics having a greater number of carbon atoms. Such processes as disclosed heretofore are, however, generally handicapped by a low yield of the olefin-substituted hydrocarbon. They generally unavoidably involve accompanying side reactions which often predominate, thereby not only producing an exceedingly low yield of the desired olefin-substituted aromatic hydrocarbon but also converting at least a substantial part of the charge to less valuable by-products. Such is the case when producing, for example, styrene from isopropyl benzene by processes disclosed heretofore. The resulting reaction product generally comprises not only an exceedingly small proportion of styrene but also

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consists predominantly of such products as alpha-methyl styrene and hydrogen, as well as considerable amounts of benzene and propylene.

It is an object of the present invention to provide an improved, continuous, unitary process for the more efficient production of olefin-substituted aromatic hydrocarbons of a lesser number of carbon atoms from alkyl aromatic hydrocarbons containing at least one alkyl group of at least three carbon atoms wherein a greater part of the alkyl aromatic hydrocarbons charged are converted to said olefin-substituted aromatic hydrocarbon.

A further object of the invention is the provision of an improved process for the more efficient production of an olefin-substituted aromatic hydrocarbon from an aykyl aromatic hydrocarbon having at least one alkyl group connected to the aromatic nucleus by carbon to carbon linkage of a secondary carbon atom in the alkyl group to a carbon atom in the aromatic nucleus.

Still another object of the invention is the provision of an improved process for the more efficient production of vinyl aromatic hydrocarbons from alkyl aromatic hydrocarbons having at least one isopropyl group directly attached to a carbon atom in the aromatic ring.

A more particular object of the invention is the provision of an improved process for the more efficient production of styrene from isopropyl benzene. Other objects and advantages of the invention will become apparent from the following detailed description thereof.

In accordance with the process of the invention an alkyl aromatic hydrocarbon containing at least one alkyl group of at least three carbon atoms is subjected to controlled destructive dehydrogenation conditions in a first conversion zone, thereby effecting the scission of an aliphatic carbon-to-carbon linkage in the substituent alkyl group with the formation of an olefin-substituted aromatic hydrocarbon containing a lesser number of carbon atoms in the aliphatic side chain than the corresponding substituent alkyl group of the alkyl aromatic hydrocarbon charged. Under the controlled destructive dehydrogenation conditions defined below, a substantial portion of the charge wil unavoidably undergo a straight dehydrogenation to the olefin-substituted aromatic hydrocarbon having the same number of carbon atoms in the substituent olefin group as the number of carbon atoms in corresponding alkyl groups of the alkyl aromatic hydrocarbon charged with the formation of by-

product hydrogen. The olefin-substituted aromatic hydrocarbon having a lesser number of carbon atoms to the molecule than the alkyl aromatic charge thus formed is separated from the effluence of the first conversion zone. At least a portion of the remainder of the effluence of the first conversion zone comprising the olefin-substituted aromatic hydrocarbon and by-product hydrogen is subjected to hydrogenating conditions in a second conversion zone, thereby saturating the olefinic side chain and reconverting the olefin-substituted aromatic hydrocarbon to the alkyl aromatic hydrocarbon originally charged. At least a portion of the effluence from the second conversion zone comprising alkyl aromatic hydrocarbon is returned to the first conversion zone.

A particular advantage of the invention resides in the ability to produce more efficiently olefin-substituted aromatic hydrocarbons having an olefinic linkage between the alpha and beta carbon atoms of the substituent olefin group from alkyl aromatic hydrocarbons containing at least one alkyl group directly connected by carbon-to-carbon linkage of a secondary carbon atom in the alkyl group to a nuclear carbon atom in the aromatic ring. When an alkyl aromatic hydrocarbon containing at least one alkyl group directly connected to the aromatic nucleus by a direct carbon-to-carbon linkage of a nuclear carbon atom with a secondary carbon atom in the alkyl group is subjected to the controlled destructive dehydrogenation conditions in the first conversion zone, there is brought about a scission of one of the alpha to beta carbon linkages in the substituent alkyl group with the formation of a reaction product comprising an olefin-substituted aromatic hydrocarbon containing an olefinic linkage between the remaining alpha and beta carbon atoms of the substituent group.

Although the process of the invention is broadly applicable to the conversion of alkyl substituted aromatic hydrocarbons to olefin-substituted aromatic hydrocarbons having a lesser number of carbon atoms to the molecule, it is preferred to use as charge the alkyl aromatic hydrocarbon having at least three but not more than six carbon atoms in the substituent alkyl side chain. Alkyl aromatics which may be converted in accordance with the process of the invention comprise, for example, isopropylbenzene, di-isopropylbenzene, n - propylbenzenes, isobutylbenzene, amylbenzenes, methyl-isopropylbenzenes, methylpropylbenzene, methylisobutylbenzene, methylbutylbenzene, butylamylbenzene, isobutyl mesitylene, isopropylisobutylbenzene, isoamylbenzene, propylmesitylene, isobutyl mesitylene, isoamylmesitylene, tert-butylbenzene and tert-p-dibutylbenzene.

As stated above, the invention is of particular value in the production of olefin-substituted aromatics having an olefinic bond between the alpha and beta carbon atoms of the substituent olefinic group from alkyl aromatics having a substituent alkyl group directly connected by carbon-to-carbon linkage of a secondary carbon atom of the alkyl group to a nuclear carbon atom of the aromatic nucleus. Examples of this preferred class of materials comprise, for example, isopropylbenzene, di-isopropylbenzene, propylisopropylbenzene, methylisopropylbenzene, 2 - phenylbutane, 2-phenylpentane, 3-phenylpentane, etc.

A particularly preferred embodiment of the invention comprises the production of vinyl aromatics from alkyl aromatic hydrocarbons containing at least one isopropyl group directly connected to the aromatic nucleus. Members of this particularly preferred group of charge material are, for example, isopropylbenzene, and the alkyl-substituted isopropylbenzenes such as methylisopropylbenzenes, di-isopropylbenzene, ethylisopropylbenzene, propyl-isopropylbenzene, etc.

The alkyl aromatics employed as charge to the process of the invention are obtained from any suitable source. They may be separated from the complex products obtained in many of the pyrogenic or catalytic hydrocarbon conversion processes, or they may be a product of synthesis such as obtained, for example, by the alkylation of an aromatic hydrocarbon with a suitable olefin. Thus isopropylbenzene is produced by the alkylation of benzene with propylene under suitable alkylating conditions and with the aid of a suitable alkylation catalyst such as, for example, sulfuric acid, aluminum chloride, phosphoric acids or the like.

The alkyl aromatic charge in the process of the invention need not necessarily consist of only a single alkyl aromatic hydrocarbon, but may comprise a mixture of two or more such hydrocarbons. The charge to the process of the invention may furthermore comprise other hydrocarbons capable or not of undergoing conversion under the conditions of execution of the process of the invention, as well as inert gaseous materials such as nitrogen, normally gaseous paraffins, steam, etc.

The controlled destructive dehydrogenation of the alkyl aromatics in the first conversion zone is obtained by the maintenance therein of well defined thermal or catalytic conditions. Suitable thermal conditions comprise a temperature in the range of from about 650° C. to about 900° C. and preferably from about 650° C. to about 850° C. The reaction zone may optionally contain suitable inert contact materials such as, for example, crushed brick, quartz chips, or the like. The residence time of reactants in the reaction zone is maintained sufficiently short to attain fission of carbon-to-carbon linkage in the alkyl chain in the absence of any substantial complete dealkylation. The residence time may range, for example, from about 0.05 second to about 5 seconds, a time of less than one second being preferred; a higher contact time may, however, be resorted to within the scope of the invention. Atmospheric or subatmospheric pressures may be resorted to. The use of relatively low superatmospheric pressures ranging, for example, from pressures slightly above atmospheric to about 100 pounds gauge are somewhat preferred. When employing the higher temperatures of the above described temperature range, diluent gases or vapors such as, for example, steam, are preferably introduced into the reaction zone.

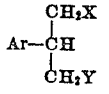
Catalytic conditions of controlled destructive dehydrogenation are preferably employed in the first conversion zone. Suitable catalysts comprise broadly the oxides or sulfides of the heavy metals, such as the oxides or sulfides of the metals of the groups V, VI and VIII of the periodic table such as, for example, the oxides and sulfides of one or more of the following: tungsten, molybdenum, chromium, vanadium, copper, iron, cobalt, nickel; solid adsorptive materials such as adsorptive alumina, activated alumina, bauxite; adsorptive siliceous materials such as the naturally occurring or synthetically produced silica-alumi-

na catalysts; mixtures of at least one of the heavy metal oxides or sulfides with an oxide of aluminum, magnesium or silicon.

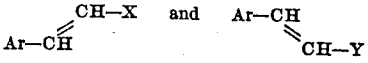
Particularly suitable catalysts comprise the adsorptive materials such as activated alumina, bauxite, activated carbon, magnesia or zirconia optionally in combination with one or more of the following: an alkaline earth metal, alkali metal, an oxide or sulfide of an alkaline earth metal or alkali metal. Preferred catalysts comprise those containing an adsorptive alumina in combination with an oxide or sulfide of calcium, lithium, strontium or cerium.

Temperatures to be maintained in the first conversion zone when resorting to the use of catalytically controlled dehydrogenation therein comprise temperatures in the range of from about 350° C. to about 750° C. and preferably from about 400° C. to about 650° C. The contact time is controlled to effect substantial fission of the alkyl side chain in the absence of any substantial complete dealkylation of the alkyl aromatic. Contact times of from about 0.1 to about 15 seconds have been found suitable. Higher contact times may, however, be resorted to within the scope of the invention. Subatmospheric, atmospheric or superatmospheric pressures may be employed when resorting to the use of catalysts. Pressures ranging from about atmospheric to about 150 pounds are, however, somewhat preferred. Introduction of diluent gases such as steam, nitrogen and the like into the catalyst-containing zone may be resorted to. The introduction of hydrogen into the first conversion zone is, however, preferably avoided since such often has been found to increase undesired side reactions such as, for example, the removal of the entire side chain from the aromatic nucleus.

Under the above-defined conditions the alkyl aromatics will undergo a destructive dehydrogenation in the first conversion zone consisting of the scission of a carbon-to-carbon linkage in the substituent alkyl chain of a portion of the alkyl aromatic charge with the formation of olefin-substituted aromatic hydrocarbons containing a lesser number of carbon atoms to the molecule than the alkyl aromatic charged. Concomitant with the destructive dehydrogenation reaction a substantial portion of the charge will undergo straight dehydrogenation of the alkyl side chain with the formation of hydrogen and an olefin-substituted aromatic having the same number of carbon atoms to the molecule as the alkyl aromatic charged. Under the prescribed destructive dehydrogenation conditions alkyl aromatics containing an alkyl chain directly connected to the aromatic nucleus by means of a secondary carbon atom in the alkyl group will undergo a fission of an alpha to beta carbon linkage resulting in the unsaturation of the remaining alpha to beta carbon linkage. Thus an aryl compound of the general formula



wherein Ar represents a benzene ring and X and Y each represent an alkyl group or hydrogen, will result in the obtaining of a reaction product comprising



wherein Ar indicates a benzene ring and X and Y each indicate an alkyl group or hydrogen. In addition to the formation of these products of lesser carbon atoms, a substantial part of the charge will undergo a straight dehydrogenation of the substituent alkyl group to result in an olefin-substituted aromatic hydrocarbon having the same number of carbon atoms as the alkyl aromatic charged and hydrogen.

Hydrogenating conditions in the second conversion zone of the process comprise the use of a suitable hydrogenation catalyst. Suitable hydrogenation catalysts comprises for example those consisting essentially of a hydrogenating metal, such as nickel, iron, cobalt and the metals of the platinum group. The hydrogenating metals may suitably be employed in combination with one or more of the difficultly reducible metal oxides such as thoria, ceria, zirconia and titania. Temperatures in the range of for example from about 25° C. to 175° C. and preferably from about 50° C. to about 125° C. and pressures in the range of from about atmospheric to 500 lbs. and preferably from about 50 to 100 lbs. have been found suitable. The invention is in no wise limited by the nature of catalyst or the specific conditions employed in the second conversion zone. The specific conditions employed therein will generally be dependent to some degree upon the particular hydrocarbon charged and the catalyst employed. Hydrogenating conditions are, however, preferably chosen which will effect the saturation of the substituent olefin group of the olefin aromatic in the absence of any substantial hydrogenation of the aromatic nucleus.

In order to set forth more fully the nature of the invention it will be described in detail herein in its application to the production of styrene from isopropylbenzene with reference to the accompanying drawing illustrating diagrammatically one form of apparatus suitable for executing the process of the invention.

Alkyl aromatic hydrocarbons comprising, for example isopropylbenzene, taken from any outside source, is forced through line 1 into a reaction zone. The reaction zone may comprise any suitable type of reactor such as, for example, an elongated externally heated coil and/or a reaction chamber of enlarged cross-sectional area. In the drawing the reaction zone is depicted by a reaction chamber 2. Within reactor 2 the isopropyl benzene is subjected to thermal or catalytic controlled destructive dehydrogenation conditions as defined above.

Preferred destructive dehydrogenating conditions comprise, for example, the use of a catalyst consisting of adsorptive alumina containing an alkaline earth metal or oxide thereof, such as for example activated alumina in combination with calcium oxide. Suitable temperatures in the range of for example from 450° C. to 750° C. are maintained in the reactor 2 by suitable heating means such as for example heater 3.

Suitable conversion of the isopropylbenzene is obtained by contact in reactor 2 with a catalyst comprising adsorptive alumina and a promoting amount of calcium oxide at a temperature in the range of from about 400° C. to about 650° C., preferably 490° C. to 590° C., and a pressure of from about atmospheric to about 150 pounds. The temperature is maintained in reactor 2 by means of any suitable heating means such as for example a heater 3. The time of contact of reactants and catalyst is maintained in the range of from about 0.02 to about 15 seconds and preferably between about 0.1 and 5 seconds.

Under these conditions demethanation of the

isopropylbenzene will occur in reactor 2 with the formation of a reaction product comprising styrene. Simultaneously with the demethanation of one portion of the charge, straight dehydrogenation of another substantial part of the isopropylbenzene charge will occur with the formation of alpha-methylstyrene and by-product hydrogen. Although the presence of the catalyst increases the total amount of charge converted, it will of necessity increase the portion of the charge undergoing straight dehydrogenation. An outstanding advantage of the invention resides in the fact that such increase in straight dehydrogenation of the charge is offset as described more fully below by substantially complete reconversion within the system of the products of the straight dehydrogenation to the starting material. The process of the invention therefore brings within the realm of practicability a full realization of the advantages inherent in the use of catalysts to effect the desired demethanation without the disadvantages encountered in processes available heretofore, involving the conversion of at least a substantial proportion of the charge material to products other than styrene.

Effluence from reactor 2 comprising styrene, alpha-methylstyrene, and hydrogen and some unconverted isopropylbenzene, is passed through line 5 into a product separating zone indicated in the drawing by fractionator 6. Within fractionator 6 a gaseous fraction comprising by-product hydrogen is separated from a liquid fraction comprising styrene, alpha-methylstyrene and isopropylbenzene. The liquid fraction is passed from fractionator 6 through line 8 into a fractionator 9. Within fractionator 9 a vapor fraction comprising styrene is separated and eliminated from the system as a final product through valved line 10. A fraction comprising isopropylbenzene and alpha-methylstyrene is separated within fractionator 9 and passed therefrom through line 12 to a fractionator 13. Any materials higher boiling than isopropylbenzene which may have been formed to some degree in the system are separated as bottoms in fractionator 9 and removed therefrom through valved line 14.

Within fractionator 13 a vapor fraction comprising isopropylbenzene is separated from a liquid fraction comprising alpha-methylstyrene. The vapor fraction is taken overhead from fractionator 13 and passed through line 16 into line 1 leading to reactor 2. The liquid fraction is taken from fractionator 13 and forced through line 17 into a second reaction zone. The second reaction zone may constitute any suitable reaction zone of elongated restricted and/or enlarged cross-sectional area. In the drawing the second reaction zone is represented by reaction chamber 18. Overhead from fractionator 6 comprising the by-product hydrogen formed in reactor 2 is forced through line 19 into reactor 18. Within reactor 18 the mixture of alpha-methylstyrene and by-product hydrogen is subjected to hydrogenating conditions effecting the hydrogenation of the alpha-methylstyrene to isopropylbenzene. Hydrogenation of the alpha-methylstyrene may be carried out under suitable hydrogenating conditions effecting the hydrogenation of alpha-methylstyrene to isopropylbenzene. Suitable hydrogenating conditions comprise, for example, the use of a catalyst comprising Raney nickel at a temperature in the range of from about 50° C. to about 100° C. and a pressure of from about 50 to about 100 pounds gauge. Although catalytic hydrogenating conditions using a Raney nickel catalyst have been set forth as suitable, it is to be stressed that the invention is in no wise limited to the use of specific hydrogenating conditions or catalysts to effect the desired hydrogenation within reactor 18. Other suitable hydrogenating catalysts comprise, for example, the heavy metal sulfides. Effective hydrogenating conditions employing a heavy metal sulfide-type catalyst comprise the use of a nickel sulfide-tungsten sulfide catalyst at a temperature of from about 250° C. to about 350° C. at a pressure of from about atmospheric to about 10 atmospheres or higher. Hydrogen produced within the system is preferably permitted to build up during the recycling thereof to attain a molar excess of hydrogen over hydrocarbons to be hydrogenated in reactor 18. Additional hydrogen from an outside source may be introduced into the system through valved line 21 when needed. Effluence from reactor 18 comprising isopropylbenzene and some unconverted alpha-methylstyrene is passed through valved line 22 into fractionator 23. Within fractionator 23 a gaseous fraction comprising residual gases formed within the system is separated from a liquid fraction comprising isopropylbenzene and alpha-methylstyrene. The liquid is passed from fractionator 23 through line 24 into fractionator 13.

Gaseous overhead is taken from fractionator 23 through valved line 25 and may be passed in part into line 19 and if desired in part into line 1. However, when the hydrogen content of the gas passing through line 25 is high, recycling thereof to reactor 2 is preferably avoided since the introduction of hydrogen into reactor 2 favors complete dealkylation of isopropylbenzene to reaction products consisting essentially of benzene and propylene, thereby seriously detracting from the efficiency of the process.

Diluent materials such as for example inert gases or steam may be introduced into the system by means of valved line 27. Elimination of gases from the system is accomplished by bleeding from valved line 28 and/or valved line 29. If desired gaseous materials may be bled from valved lines 28 and/or 29 and subjected in part or entirety to a purification or separation process and a portion of the thus treated gas returned into the system.

It is seen from the foregoing that the unitary process of the invention provides a method for the substantially complete conversion in a continuous highly efficient operation of substantially all of the alkyl aromatic hydrocarbon charged to the system to a final product consisting essentially only of olefin-substituted aromatic hydrocarbon containing a lesser number of carbon atoms to the molecule than the hydrocarbon charge. The process of the invention, because of its complete utilization within the system of the products of straight dehydrogenation, unavoidably encountered to a substantial degree, enables the full realization of the advantages inherent in the use of dehydrogenation catalysts to obtain the desired controlled destructive dehydrogenation without the substantial loss of charge material encountered in the production of olefin aromatics from alkyl aromatics of a greater number of carbon atoms by methods available heretofore.

The following examples further illustrate the process of the invention:

Example I

Isopropylbenzene is charged to a first reaction zone consisting of an externally heated unpacked

tubular reactor wherein it is subjected to a temperature of about 750° C. for a period of 0.1 second at substantially atmospheric pressure. Effluence from the first reactor is passed through a cooler into a first product separating zone consisting of a series of fractionators wherein a gaseous fraction consisting essentially of hydrogen and liquid fractions consisting essentially of styrene and alpha-methylstyrene respectively are separated from the reaction products. The alpha-methylstyrene and normally gaseous fractions are passed into a second conversion zone consisting of a reaction chamber equipped with stirring means. In the second reactor the alpha-methylstyrene-hydrogen mixture is subjected to catalytic hydrogenating conditions in the temperature range of from 50° C. to 100° C., and a pressure of about 70 pounds in the presence of a Raney nickel catalyst. A contact time in the range of from about 5 to 12 minutes is maintained. Effluence from the second reaction zone is passed through a cooler into a fractionator wherein a normally gaseous fraction is separated from a liquid fraction consisting of isopropylbenzene and unconverted alpha-methylstyrene. The liquid fraction consisting of isopropylbenzene and alpha-methylstyrene is recycled to the first product separating zone. Hydrogenation within the system of substantially all by-product alpha-methylstyrene to isopropylbenzene is attained. A conversion per pass of isopropylbenzene of 68% is obtained in the first reactor with a yield of 33% styrene and 20% alpha-methylstyrene.

Example II

Isopropylbenzene is subjected to catalytic demethanation in a first reactor by contact with a catalyst consisting of calcium-promoted activated alumina at substantially atmospheric pressure. The temperature in the first reactor is maintained in the range of from 550° C. to 560° C. Steam is added to the ispropylbenzene charge and the mixture introduced into the first reactor at a rate of 50 mols of ispropylbenzene and 100 mols of steam per liter of catalyst per hour. Effluence from the first reactor is passed through a cooler into a first product separating zone consisting of a series of fractionators wherein a gaseous fraction consisting essentially of hydrogen and two liquid fractions consisting essentially of styrene and alpha-methylstyrene, respectively, are separated from the reaction products. The alpha-methylstyrene and normally gaseous fractions are passed into a second conversion zone consisting of a reaction chamber equipped with stirring means. In the second reactor the alpha-methylstyrene-hydrogen mixture is subjected to catalytic hydrogenating conditions in the temperature range of from 50° C. to 100° C. and a pressure of about 70 pounds in the presence of a Raney nickel catalyst. A contact time in the range of from about 5 to 12 minutes is maintained. Effluence from the second reaction zone is passed through a cooler into a fractionator wherein a normally gaseous fraction is separated from a liquid fraction consisting of isopropylbenzene and unconverted alpha-methylstyrene. The liquid fraction consisting of isopropyl-benzene and alpha-methylstyrene is recycled to the first product separating zone. Hydrogenation within the system of substantially all by-product alpha-methylstyrene to isopropylbenzene is attained. A conversion per pass of isopropylbenzene of 19.5% is obtained in the first reactor with a yield of 32% styrene and 16% alpha-methylstyrene.

Example III

In a repetition of the process of Example II under substantially identical conditions but with the exception that a catalyst consisting of adsorptive alumina is employed in the first reactor at a temperature of 650° C., a conversion per pass of ethyl isopropylbenzene of 58% is obtained in the first conversion zone with a yield of 11% styrene and 62% alpha-methylstyrene.

Example IV

In a repetition of the process of Example II under substantially identical conditions but with the use of another calcium-promoted adsorptive alumina catalyst at a temperature of 650° C. in the first reactor a conversion per pass of isopropylbenzene of 49% is obtained in the first conversion zone with a yield of 12% styrene and 65% alpha-methylstyrene.

In the foregoing examples, because of the continuous reconversion of the by-product hydrogen and alpha-methylstyrene to isopropylbenzene and the reintroduction of the latter into the controlled destructive dehydrogenation zone, an ultimate reaction product consisting essentially of styrene is obtained.

Similarly alkyl-substituted styrenes are produced from the corresponding alkyl-substituted ispropylbenzenes. Thus p-methylstyrene is produced in accordance with the process of the invention from cymene, the asym. methyl p-tolylethylene simultaneously produced in the destructive dehydrogenation zone being continuously hydrogenated to cymene within the system, as exemplified by the following example:

Example V

Cymene is subjected to catalytic demethanation in a first reactor by contact with a catalyst consisting of calcium-promoted activated alumina at substantially atmospheric pressure at a temperature of about 730° C. 1.5 mols of steam per mol of cymene charge is employed and the mixture passed through the first reactor at the rate of 2.5 mols of the cymene-steam mixture per liter of catalyst per hour. Effluence from the first reactor is passed through a cooler into a first product separating zone consisting of a series of fractionators wherein a gaseous fraction consisting essentially of hydrogen and two liquid fractions consisting essentially of p-methylstyrene and asym. methyl p-tolylethylene, respectively, are separated from the reaction products. The asym. methyl p-tolylethylene and normally gaseous fractions are introduced into a second conversion zone wherein they are contacted with a nickel-tungsten-sulfide catalyst at a pressure of 4.5 atmospheres and a temperature of about 300° C. at a liquid hourly space velocity of 2. Effluence from the second reaction zone is passed through a cooler into a fractionator wherein a normally gaseous fraction is separated from a liquid fraction comprising cymene and unconverted asym. methyl p-tolylethylene. The liquid fraction consisting of cymene and asym. methyl p-tolylethylene is recycled to the first product separating zone. Hydrogenation of substantially all by-product asym. methyl p-tolylethylene to cymene is attained within the system. A conversion per pass of cymene of 60% is obtained in the first conversion zone.

The invention claimed is:

1. A process for the production of styrene

which comprises subjecting isopropylbenzene to destructive dehydrogenating conditions in a first conversion zone, thereby effecting the conversion of isopropylbenzene to a reaction product comprising styrene, alpha-methylstyrene and hydrogen in said first conversion zone, separating styrene from the effluence of said first conversion zone, subjecting the remaining effluence of said first conversion zone to hydrogenating conditions in a second conversion zone, thereby effecting the hydrogenation of alpha-methylstyrene to isopropylbenzene in said second conversion zone, and passing effluence from said second conversion zone to said first conversion zone.

2. A process for the production of styrene which comprises subjecting isopropylbenzene to destructive dehydrogenating conditions at a temperature of from about 350° C. to about 750° C. in the presence of a dehydrogenation catalyst in a first conversion zone, thereby effecting the conversion of isopropylbenzene to a reaction product comprising styrene, alpha-methylstyrene and hydrogen in said first conversion zone, separating hydrocarbons comprising styrene from the effluence of said first conversion zone, subjecting at least a part of the remaining effluence of said first conversion zone to hydrogenating conditions in a second conversion zone, thereby effecting the hydrogenation of alpha-methylstyrene to isopropylbenzene in said second conversion zone, and passing at least a part of the effluence from said second conversion zone to said first conversion zone.

3. A process for the production of styrene which comprises subjecting isopropylbenzene to destructive dehydrogenating conditions at a temperature of from about 400° C. to about 650° C. in the presence of a dehydrogenation catalyst in a first conversion zone, thereby effecting the conversion of isopropylbenzene to a reaction product comprising styrene, alpha-methylstyrene and hydrogen in said first conversion zone, separating a fraction comprising styrene from the effluence of said first conversion zone, subjecting the remaining effluence of said first conversion zone to hydrogenating conditions in a second conversion zone, thereby effecting the hydrogenation of alpha-methylstyrene to isopropylbenzene in said second conversion zone, and passing effluence from said second conversion zone to said first conversion zone.

4. A process for the production of styrene which comprises subjecting hydrocarbons comprising isopropylbenzene to destructive dehydrogenating conditions at a temperature of from about 400° C. to about 650° C. in the presence of a dehydrogenation catalyst comprising adsorptive alumina in a first conversion zone, thereby effecting the conversion of isopropylbenzene to a reaction product comprising styrene, alpha-methylstyrene and hydrogen in said first conversion zone, separating a fraction comprising styrene from the effluence of said first conversion zone, subjecting the remaining effluence of said first conversion zone to hydrogenating conditions in a second conversion zone, thereby effecting the hydrogenation of alpha-methylstyrene to isopropylbenzene in said second conversion zone, and passing effluence from said second conversion zone to said first conversion zone.

5. A process for the production of styrene which comprises subjecting isopropylbenzene to thermal destructive dehydrogenating conditions at a temperature of from about 650° C. to about 900° C. and a residence time of from about 0.05 to about 5 seconds in a first conversion zone, thereby effecting the conversion of isopropylbenzene to a reaction product comprising styrene, alpha-methylstyrene and hydrogen in said first conversion zone, separating styrene from the effluence of said conversion zone, subjecting at least a part of the remaining effluence of said first conversion zone to hydrogenating conditions in a second conversion zone, thereby effecting the hydrogenation of alpha-methylstyrene to isopropylbenzene in said second conversion zone, and passing effluence from said second conversion zone to said first conversion zone.

6. A process for the production of vinyl-substituted aromatic hydrocarbons which comprises subjecting alkyl aromatics having at least one substituent isopropyl group directly attached to the aromatic nucleus to destructive dehydrogenating conditions in a first conversion zone, thereby effecting the conversion of said alkyl aromatics to a reaction product comprising vinyl aromatics, olefin-substituted aromatics having the same number of carbon atoms as said alkyl aromatic charge and hydrogen in said first conversion zone, separating vinyl aromatics from the effluence of said first conversion zone, subjecting the remaining effluence of said first conversion zone to hydrogenating conditions in a second conversion zone, thereby effecting the hydrogenation of olefin-substituted aromatics to alkyl aromatics in said second conversion zone, and passing effluence from said second conversion zone to said first conversion zone.

7. A process for the production of vinyl-substituted aromatic hydrocarbons from alkyl aromatic hydrocarbons having at least one substituent isopropyl group directly attached to the aromatic nucleus which comprises subjecting alkyl aromatics having at least one substituent isopropyl group directly attached to the aromatic nucleus to destructive dehydrogenating conditions at a temperature in the range of from about 350° C. to about 750° C. in the presence of a dehydrogenation catalyst in a first conversion zone, thereby effecting the conversion of said alkyl aromatics to a reaction product comprising olefin-substituted aromatics having the same number of carbon atoms as the alkyl aromatic charge, vinyl-substituted aromatics and hydrogen in said first conversion zone, separating vinyl-substituted aromatic hydrocarbons from the effluence of the first conversion zone, subjecting the remainder of said effluence of the first conversion zone to hydrogenating conditions in a second conversion zone, thereby effecting the conversion of olefin-substituted aromatics to alkyl aromatics in said second conversion zone, and passing at least a part of the effluence of said second conversion zone to said first conversion zone.

8. A process for the production of olefin-substituted aromatic hydrocarbons containing a lesser number of carbon atoms from alkyl aromatic hydrocarbons containing a greater number of carbon atoms which comprises subjecting alkyl aromatic hydrocarbons having a substituent alkyl group of at least three carbon atoms connected by a secondary carbon atom in the alkyl group to a carbon atom in the aromatic nucleus to destructive dehydrogenating conditions in a first conversion zone, thereby effecting the conversion of alkyl aromatic hydrocarbons to a reaction product comprising olefin-substituted aromatics having the same number of carbon atoms as said alkyl aromatic charge, olefin-substituted aromatic hydrocarbons having a lesser number of carbon atoms than said alkyl aromatic charge

and hydrogen in said first conversion zone, separating olefin-substituted aromatic hydrocarbons having a lesser number of carbon atoms than said alkyl aromatic charge from the effluence of said first conversion zone, subjecting at least a part of the remaining effluence of said first conversion zone to hydrogenating conditions in a second conversion zone, thereby effecting the hydrogenation of olefin-substituted aromatic hydrocarbons to alkyl aromatic hydrocarbons in said second conversion zone and passing effluence from said second conversion zone to said first conversion zone.

9. A process for the production of olefin-substituted aromatic hydrocarbons having a lesser number of carbon atoms to the molecule from alkyl aromatic hydrocarbons having a greater number of carbon atoms to the molecule which comprises subjecting alkyl aromatics having at least one substituent alkyl group of at least three carbon atoms connected by a secondary carbon atom in the alkyl group to a carbon atom in the aromatic nucleus to destructive dehydrogenating conditions at a temperature in the range of from about 350° to about 750° C. in the presence of a dehydrogenation catalyst in a first conversion zone, thereby effecting the conversion of alkyl aromatics to a reaction product comprising olefin-substituted aromatics having the same number of carbon atoms as the alkyl aromatic charge, olefin-substituted aromatics having a lesser number of carbon atoms than the alkyl aromatic charge and hydrogen in said first conversion zone, separating olefin-substituted aromatic hydrocarbons having a lesser number of carbon atoms than the aromatic charge from the effluence of the first conversion zone, subjecting the remainder of said effluence of the first conversion zone to hydrogenating conditions in a second conversion zone, thereby effecting the conversion of olefin-substituted aromatics to alkyl aromatics in said second conversion zone, and passing at least a part of the effluence of said second conversion zone to said first conversion zone.

10. A process for the production of olefin-substituted aromatic hydrocarbons having a lesser number of carbon atoms to the molecule from alkyl aromatic hydrocarbons having a greater number of carbon atoms to the molecule which comprises subjecting alkyl aromatics having at least one substituted alkyl group of at least three carbon atoms to destructive dehydrogenating conditions in a first conversion zone, thereby effecting the conversion of alkyl aromatics to a reaction product comprising olefin-substituted aromatics having the same number of carbon atoms as the alkyl aromatic charge, olefin-substituted aromatics having a lesser number of carbon atoms than the alkyl aromatic charge and hydrogen in said first conversion zone, separating olefin-substituted aromatic hydrocarbons having a lesser number of carbon atoms than the aromatic charge from the effluence of the first conversion zone, subjecting the remainder of said effluence of the first conversion zone to hydrogenating conditions in a second conversion zone, thereby effecting the conversion of olefin-substituted aromatics to alkyl aromatics in said second conversion zone, and passing at least a part of the effluence of said second conversion zone to said first conversion zone.

11. A process for the production of olefin-substituted aromatic hydrocarbons having a lesser number of carbon atoms to the molecule from alkyl aromatic hydrocarbons having a greater number of carbon atoms to the molecule which comprises subjecting alkyl aromatics having at least one substituent alkyl group of at least three carbon atoms to thermal destructive dehydrogenating conditions at a temperature in the range of from about 650° C. to about 900° C. and a residence time of from about 0.05 to about 5 seconds in a first conversion zone, thereby effecting the conversion of alkyl aromatics to a reaction product comprising olefin-substituted aromatics having the same number of carbon atoms as the alkyl aromatic charge, olefin-substituted aromatics having a lesser number of carbon atoms than the alkyl aromatic charge and hydrogen in said first conversion zone, separating olefin-substituted aromatic hydrocarbons having a lesser number of carbon atoms than the aromatic charge from the effluence of the first conversion zone, subjecting the remainder of said effluence of the first conversion zone to hydrogenating conditions in a second conversion zone, thereby effecting the conversion of olefin-substituted aromatics to alkyl aromatics in said second conversion zone, and passing at least a part of the effluence of said second conversion zone to said first conversion zone.

12. A process for the production of olefin-substituted aromatic hydrocarbons having a lesser number of carbon atoms to the molecule from alkyl aromatic hydrocarbons having a greater number of carbon atoms to the molecule which comprises subjecting alkyl aromatics having at least one substituent alkyl group of at least three carbon atoms to destructive dehydrogenating conditions at a temperature in the range of from about 350° C. to about 750° C. in the presence of a dehydrogenation catalyst in a first conversion zone, thereby effecting the conversion of alkyl aromatics to a reaction product comprising olefin-substituted aromatics having the same number of carbon atoms as the alkyl aromatic charge, olefin-substituted aromatics having a lesser number of carbon atoms than the alkyl aromatic charge and hydrogen in said first conversion zone, separating olefin-substituted aromatic hydrocarbons having a lesser number of carbon atoms than the aromatic charge from the effluence of the first conversion zone, subjecting the remainder of said effluence of the first conversion zone to hydrogenating conditions in a second conversion zone, thereby effecting the conversion of olefin-substituted aromatics to alkyl aromatics in said second conversion zone, and passing at least a part of the effluence of said second conversion zone to said first conversion zone.

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