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PROCESS FOR ALKYLATING AROMATIC
HYDROCARBONS

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This invention relates to an improved process for the manufacture of alkyl aryl compounds and is more particularly concerned with a process for producing straight chain alkylbenzenes with a relatively low 2-phenyl isomer content.

Alkylbenzene sulfonates are widely used by soap manufacturers in their commercial detergent products. These alkylbenzene sulfonates are generally prepared by alkylating benzene with olefins followed by sulfonation and neutralization. Generally speaking when the olefin used is of a straight chain structure the resulting alkylbenzene products are comprised of a mixture of isomers according to the position of the phenyl group on the alkyl chain. It is known in the art that the position of the phenyl group on the alkyl chain is an important factor in determining the surface active properties of the resulting alkylbenzene products. In general when the alkyl group is of a straight chain structure containing of from about 12 to 14 carbon atoms per molecule the preferred alkylbenzene products are those in which the phenyl group is attached in the vicinity of the center of the alkyl chain, that is, the 3, 4, 5, 6, and 7-phenyl isomers. In addition, when alkylating with a catalyst, such as aluminum chloride and hydrogen chloride, which is believed to function in the synthesis by converting the olefin into a carbonium ion, the 1-phenyl isomer is not formed while the 2-phenyl isomer is oftentimes formed to the extent of 35 to 40% of the total phenyl distribution. It is further known that the 2-phenyl isomer sulfonate product is objectionable because of its relatively low water solubility.

It is also known that in the alkylation of benzene with a straight chain olefin using aluminum chloride and hydrogen chloride as the catalyst is formed alkylbenzenes containing a 2-phenyl isomer content greater than about 32% of the total phenyl distribution. The prior art points out that depending upon, inter alia, the sojourn of alkylation and the ratio of catalyst to olefin used, there exists an equilibrium distribution of the various isomers of alkylbenzenes with about 32% being the equilibrium distribution and the minimum 2-phenyl isomer content formed.

As can be appreciated, therefore, a method for producing straight chain alkylbenzenes in which the phenyl group is attached in the vicinity of the center of the alkyl group and herein denoted as containing a relatively low 2-phenyl isomer content, that is, one containing substantially less than the 2-phenyl isomer content obtained under normal alkylation conditions, would represent a significant advancement in this art.

It is, therefore, an object of this invention to provide a process for producing straight chain alkyl aryl compounds which contain a relatively low proportion of the isomer wherein the aryl nucleus is attached at the two position of the alkyl chain.

It is a further object of this invention to provide a process for producing straight chain alkylbenzenes with a relatively low 2-phenyl isomer content.

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It is a further object of this invention to provide a process for preparing straight chain alkylbenzenes with a relatively low 2-phenyl isomer content which are especially well suited for use as detergents when further processed into alkylbenzene sulfonates.

These and other objects will become apparent from a reading of the following detailed description and claims.

It has now been found that straight chain alkylbenzenes containing a relatively low 2-phenyl isomer content can be prepared by isomerizing straight chain alpha-olefins, wherein any suitable isomerization catalyst may be used, and utilizing the isomerized olefins by alkylating with benzene in the presence of a Friedel-Crafts catalyst. Further reduction in the 2-phenyl content may be obtained by using a catalyst modifier in combination with an appropriate Friedel-Crafts catalyst in the alkylation step. This ability to reduce the 2-phenyl isomer content is surprising and totally unexpected especially with an alkylation catalyst such as HCl activated aluminum chloride in view of the ascertainment by the prior art, supra, of an equilibrium distribution of 32% for the 2-phenyl isomer. In general, by following the teachings of the instant invention it is possible to reduce the 2-phenyl content of the alkylbenzenes about 5 percentage points from that obtained from normal alkylation by the practice of isomerizing the alpha-olefins prior to alkylation and it is further possible to reduce the 2-phenyl isomer content of the alkylbenzenes about 10 percentage points from that obtained from normal alkylation by the practice of isomerizing the alpha-olefins and thereafter alkylating in the presence of an appropriate Friedel-Crafts catalyst and catalyst modifier combination. All of the foregoing will be more fully discussed hereinafter. As can be appreciated such a reduction in the 2-phenyl isomer content of the resulting alkylbenzenes represents a significant decrease and produces alkylbenzenes which when further processed into an alkylbenzene sulfonate results in a superior detergent product.

Olefins which are suitable for use in the instant invention are high molecular weight straight chain olefins containing a high percentage by weight of alpha olefins, that is to say, substantially more than 10% by weight of alpha olefins, and herein denoted as straight chain alpha olefins, such as those obtained from such sources as petroleum wax, fat derived alcohols and ethylene polymerization. Straight chain alpha-olefins containing from about 6 to 20 carbon atoms are preferred and can be the relatively pure alpha-olefins, such as 1-dodecene, or a mixture of alpha-olefins, such as C₁₀-C₁₇ mixture averaging about 12 to 14 carbon atoms per molecule. Because of their relatively inexpensiveness, availability and their ability to produce a superior detergent product the alpha-olefin C₁₀-C₁₇ mixture and averaging about 12 to 14 carbon atoms per molecule is especially preferred.

The isomerization of the straight chain alpha-olefins can be carried out by various means which include vapor phase catalytic isomerization and liquid phase catalytic isomerization. By vapor phase catalytic isomerization is meant the catalytic isomerization of the olefins in the vapor phase and includes the use of such catalysts as alumina, chromia-alumina, and magnesia-alumina. By liquid phase catalytic isomerization is meant the catalytic isomerization of the olefins in the liquid phase and includes the use of such catalysts as sodium-alumina, potassium alumina and certain synthetic resin catalysts,

such as, the sulfonic acid resin "Amberlyst-15" sold commercially by Rohm and Haas Company.

It should be noted, however, that, except as may be specified in the appended claims, the invention is not to be limited to any particular isomerization catalyst and that although best results for reducing the 2-phenyl isomer content are usually achieved when utilizing isomerized olefins wherein substantially all of the olefins have been converted from alpha-olefins to those containing more centrally bonded olefin position isomers, it nevertheless may be advantageous at times to merely isomerize the alpha-olefins short of complete conversion. Therefore, when alkylating straight chain olefins with benzene under normal alkylation conditions and in the presence of a Friedel-Crafts catalyst the straight chain olefins should contain not more than 10% by weight of alpha-olefins in order to achieve significant results in reducing the 2-phenyl isomer content of the alkylbenzenes formed. In this connection it should be noted that when straight chain olefins containing about 45% by weight of alpha-olefins were alkylated with benzene under normal alkylation conditions and in the presence of a HCl activated aluminum chloride catalyst the resulting alkylbenzenes had a 2-phenyl isomer content of about 36% which, of course, is about the same 2-phenyl content achieved when alkylating substantially pure alpha-olefins, and, therefore, represents no 2-phenyl isomer content reduction. However, when alkylating straight chain olefins with benzene in the presence of an appropriate Friedel-Crafts catalyst and catalyst modifier the straight chain olefins may contain an appreciable alpha-olefin content but should not contain more than about 50% by weight of alpha-olefins in order to achieve significant results in reducing the 2-phenyl isomer content of the alkylbenzenes formed.

Since alkylbenzene is most commonly used in the preparation of detergents, the instant invention is disclosed with reference to a process for the manufacture of those products although it will be apparent that it may be equally advantageously employed to prepare other alkyl aryl compounds. For example, phenol, toluene, naphthalene and xylene are exemplary but not limitative of the aromatic compounds which are suitable for use in the compound.

In general, alkylation conditions, such as catalyst to olefin ratio, benzene to olefin ratio, sojourn and temperature appear to have little or no effect on the 2-phenyl isomer content when practicing the present invention although these conditions are extremely important with respect to the efficiency of alkylation and optimum product recovery. However, when using a Friedel-Crafts catalyst such as the HCl activated aluminum chloride catalyst, it should be noted that relatively high catalyst to olefin ratios are conducive to forming the aforementioned equilibrium distribution and should not be employed. Therefore, it is preferred that substantially normal alkylation conditions which for the aluminum chloride-HCl catalyst system is a catalyst to olefin molar ratio within the range of about 1:15 to 1:30 with about 1:20 being preferred, a benzene to olefin molar ratio within the range of about 3:1 to 10:1 with about 6:1 being preferred, a sojourn within the range of between about 5 to 60 minutes with about 15 minutes being preferred, and a temperature within the range of about 25° C. to 75° C. with about 30° C. being preferred, can be used when practicing this invention. It should further be noted, that when using the catalyst modifier with an appropriate Friedel-Crafts catalyst the molar ratio of catalyst to olefin should preferably be increased over that normally used in order to carry the alkylation to completion and for this catalyst system, such as aluminum chloride-HCl catalyst in combination with nitromethane as the catalyst modifier, the ratio of modified catalyst to olefin of at least about 2:1 and preferably not over 10:1

is generally suitable with a ratio of about 5:1 being especially preferred. In most instances molar ratios in excess of 10:1 and even as high as about 50:1 may be used, however, the use of the higher molar ratios of modified catalyst to olefin does not appear to offer any significant advantages over the use of the lower molar ratios. It should also be noted that as used herein "sojourn" is meant the time period inclusive of addition of the reactants and catalyst into the alkylation zone to the termination of agitation and the alkylation reaction.

Any Friedel-Crafts catalyst, that is, one which functions by the mechanism of the olefin forming an intermediate carbonium ion, is suitable for use in this process. As being representative of such catalysts the following are included: activated aluminum chloride, activated aluminum bromide, hydrogen fluoride, boron trifluoride, a combination of hydrogen fluoride and boron trifluoride, and sulfuric acid. The foregoing aluminum halide catalysts may be activated by a hydrogen halide or in some instances water. However, the aluminum chloride activated by HCl is the preferred catalyst for the alkylation step in the present invention.

As previously mentioned, the 2-phenyl isomer content can be reduced even further from that obtained by alkylating the isomerized olefins in the presence of a Friedel-Crafts catalyst when using a catalyst combination comprised of an appropriate Friedel-Crafts catalyst and a catalyst modifier. Appropriate Friedel-Crafts catalysts are those catalysts which are believed to form complexes with the catalyst modifier and which include activated aluminum chloride, activated aluminum bromide and boron trifluoride. The catalyst modifiers suitable for use are organo-nitro compounds and include nitroparaffins, such as, nitromethane, nitroethane and 1-nitropropane, and nitro-aromatics, particularly mono-cyclic nitro-substituted aromatic compounds such as, nitrobenzene and nitrotoluene, with nitromethane and nitrobenzene being preferred and nitromethane being especially preferred. In general the catalyst modifier may be used in molar ratios of modifier to catalyst of at least about 1:1 and preferably not over 5:1 with the molar ratio of about 2:1 being especially preferred. In most instances molar ratios in excess of about 5:1 and even as high as about 25:1 may be used, however, the use of the higher molar ratios of modifier to catalyst does not appear to offer any significant advantages over the use of the lower molar ratios. The catalyst modifier may be added to the catalyst prior to introduction into the alkylation zone or may be added prior to or subsequent to the addition of the catalyst into the alkylation zone. However, if the alkylation is a batch process it is preferred to introduce the catalyst modifier into the reaction zone prior to the addition of the catalyst especially when using a catalyst such as aluminum chloride activated with HCl because of the exothermic heat of mixing which the catalyst undergoes with the reactants. In a continuous process it is usually preferred to combine the catalyst and catalyst modifier prior to their introduction into the alkylation zone.

To illustrate the invention the following examples are presented with parts by weight being used unless otherwise indicated.

ISOMERIZATION

For example purposes the following is a description of the procedure for vapor phase catalytic isomerization and liquid phase catalytic isomerization.

Example I

For vapor phase isomerization the catalyst bed (a column 1" in diameter and 9" long) was placed in the reactor and activated at about 400° C. under a stream of dry nitrogen for about 12 to 24 hours. After the catalyst bed was activated the temperature of the vaporizer and reactor were adjusted to the indicated temperatures, nitrogen flow was stopped and the olefin, vaporized in the

vaporizer at the indicated temperature, was started flowing. The indicated feed rate was the rate of liquid olefin

The following table summarizes the results of the various isomerizations and the extent of isomerization.

TABLE II

Type catalyst	Type olefin	1-olefin remaining (percent by weight)
(1) Sodium-alumina.....	C ₁₁ -C ₁₄ straight chain alpha-olefin..	<1
(2) Sodium-alumina.....	1-dodecene.....	<1
(3) "Amberlyst-15".....	C ₁₁ -C ₁₄ straight chain alpha-olefin..	<5

to the vaporizer. Material collected during the first half hour was discarded as not being representative of equilibrium conditions.

The extent of isomerization was determined by infrared analysis with alpha-olefins giving a characteristic absorption band at 905 cm.⁻¹.

The following table summarizes the results of various isomerizations and the extent of isomerization with the variables as noted.

TABLE I

Type ¹ catalyst	Type olefin	Feed rate (ml./min.)	Temperature vaporizer, (° C.)	Temperature reactor, (° C.)	1-olefin remaining (percent by weight)
(1) Alumina.....	C ₁₁ -C ₁₄ straight chain alpha-olefin..	1.08	372	376	45
(2) Chromia-alumina.....	C ₁₁ -C ₁₄ straight chain alpha-olefin..	1.08	332-342	370-375	1.4
(3) Magnesia-alumina.....	C ₁₁ -C ₁₄ straight chain alpha-olefin..	1.08	350	377	.7

¹ Alumina catalyst used was A1-0104-T, 1/8" dia., sold by Harshaw Chemical Company. Chromia-alumina catalyst used was Cr-1404 T, 1/8" dia., sold by Harshaw Chemical Company. Magnesia-alumina catalyst used was 10% Mg with approximate formula MgO (Al₂O₃)₇.

As can be observed from the above table isomerizations with each type of catalyst resulted in reducing the 1-olefin isomer content to below 50% of the total isomer distribution. In addition, when using the catalysts chromia-alumina and magnesia-alumina the isomerization resulted in essentially eliminating the 1-olefin isomer content by reducing it to below 2% of the total isomer distribution.

Example II

For sodium-alumina liquid phase isomerization the alumina, 609 parts, was activated by heating to about 400° C. for a period of about 12 hours. The activated alumina was then charged to a reaction vessel equipped with paddle stirrer, thermocouple, and nitrogen pump. The vessel was dried by heating to about 120° C. under a dry nitrogen stream for about 5 hours. When the alumina cooled to about 150° C., metallic sodium, about 94 parts, was added with stirring at such a rate that the temperature did not exceed about 180° C. After the sodium-alumina catalyst was allowed to cool to about 110° C., the olefin, about 1608 parts, was added over a period of about 5 minutes. The olefin was stirred with the catalyst for about 60 hours at about 120° C., then decanted from the catalyst and added to a fresh charge of activated sodium-alumina catalyst and stirred with the catalyst for about 20 hours at about 120° C.

For "Amberlyst-15" liquid phase isomerization the olefin was preheated to about 125 to 135° C. and charged in an amount of about 120 parts to a reaction vessel equipped with paddle stirrer. The resin, about 9.5 parts was charged to the vessel. The mixture was maintained at about 125 to 135° C. for about 120 minutes with constant stirring. The mixture was then allowed to cool to room temperature and filtered to separate the olefin and resin.

The extent of isomerization was determined by infrared analysis with alpha-olefins giving a characteristic absorption at 905 cm.⁻¹.

As can be observed from the above table isomerizations with each type of catalyst resulted in reducing the 1-olefin content to below about 5%, thus essentially eliminating the 1-olefin isomer.

ALKYLATION

Example III

The aluminum chloride-HCl catalyzed alkylations were carried out in a reaction vessel equipped with stirrer,

thermometer, and sample port. The benzene was charged to the reactor and saturated with anhydrous HCl. The catalyst modifier, when used, was then added followed by the catalyst, AlCl₃. The reaction mixture was adjusted to the desired temperature and the olefins added to the stirred mixture over about a 2 to 3 minute period. The reaction mixture was maintained at the desired temperature with external cooling. The aging period varied as indicated from 0 to about 90 minutes. Upon settling, two layers quickly formed with the top layer being the alkylated liquor layer and the bottom layer being the catalyst layer. The alkylated liquor was separated from the catalyst layer and analyzed.

The hydrogen fluoride catalyzed alkylations were carried out in an alkylator equipped with a stirrer, thermocouple, cooling coil and sample port. The benzene and hydrogen fluoride were charged in the indicated proportions to the alkylator. The olefins were added over a period of about 5 to 10 minutes while the mixture was maintained at the indicated temperatures. The reaction mixture was stirred for an additional 15 minutes, then allowed to settle. The catalyst phase separated as a lower layer from the alkylated liquor phase. The layers were separated and the alkylated liquor was washed with caustic and then water and analyzed.

The isomer distribution analyses were determined by vapor phase chromatography of the washed alkylated liquor. The instrument used was a Barber-Coleman Model 20 Chromatograph equipped with a Sr-90 ionization detector and coupled integrator. The column used was a 150' x .02" stainless steel capillary coated with SE-30 Silicon Gum Rubber. Column temperature and pressure used for the analyses were 188° C. and 4 to 5 p.s.i.g. Calculations of the percent 2-phenyl isomer were made on the basis of the integrator count after compensating for base line corrections.

The following table summarizes the results of various alkylations and isomer distribution analyses with the variables used as noted.

TABLE III

Type Olefin	A Catalyst/ olefin (molar ratio)	B Modifier/ catalyst (molar ratio)	Benzene/ olefin (molar ratio)	Temperature (° C.)	Sojourn (min.)	C Percent 2-phenyl
(1) 1-dodecene.....	1:20	-----	10:1	25	15	37.3
(2) C ₁₁ -C ₁₄ straight chain alpha-olefin....	1:30	-----	7:1	25	15	38.3
(3) Isomerized dodecene.....	1:20	-----	10:1	25	15	29.7
(4) Isomerized C ₁₁ -C ₁₄ straight chain olefin.....	1:30	-----	7:1	25	15	27.6
(5) Isomerized C ₁₁ -C ₁₄ straight chain olefin.....	5:1	2:1	10:1	26	15	21.8
					30	22.0
					60	21.5
					90	21.7
(6) Isomerized dodecene.....	5:1	2:1	10:1	25	15	21.0
(7) C ₁₀ -C ₁₃ straight chain alpha-olefin....	15:1	-----	10:1	6	20	18.3
(8) 1-dodecene.....	15:1	-----	10:1	6	20	18.4
(9) C ₁₁ -C ₁₄ isomerized straight chain olefin.....	15:1	-----	10:1	6	20	13.5

A. Alkylations (1) through (6) were aluminum chloride-HCl catalyzed alkylations; (7) through (9) were hydrogen fluoride catalyzed.

B. Modifier used was nitro methane.

C. % 2-phenyl for alkylations (7) through (9) are reported as % 2-phenyl in C-12 fraction of alkyl benzene.

As can be observed from the above table normal alkylations using an aluminum chloride activated by HCl catalyst, i.e., (1) and (2), resulted in a percent 2-phenyl isomer content of about 38, while using a hydrogen fluoride catalyst, i.e., (7) and (8), resulted in a percent 2-phenyl isomer content of about 18. However, when in each case the alpha-olefins were isomerized prior to alkylation, i.e., (3), (4), and (9), the percent 2-phenyl isomer content was reduced by 5 or more percentage points of the total isomer distribution. In addition, when the alpha-olefins were isomerized and thereafter alkylated with an appropriate Friedel-Crafts catalyst-catalyst modifier combination, i.e., (5) and (6), the percent 2-phenyl isomer content was reduced by over 10 percentage points of the total isomer distribution from that obtained under normal alkylating conditions, i.e., (1) and (2). As can be appreciated, therefore, the above data dramatically illustrates the effect on the percent 2-phenyl isomer content when practicing the instant invention.

Although the present invention has been described with a great deal of specificity and particularity, the only limitations intended are those appearing within the appended claims.

What is claimed is:

1. In an alkylation process for producing straight chain alkyl aryl compounds wherein the aromatic nuclei of the aromatic compounds are alkylated using straight chain olefins, the improvement which comprises alkylating straight chain olefins containing not more than about 50% by weight of alpha olefins with aromatic compounds in the presence of alkylation catalyst combination of a Friedel-Crafts catalyst selected from the class consisting of activated aluminum chloride, activated aluminum bromide, and boron trifluoride, and an organo-nitro catalyst modifier, said alkylation conducted with a catalyst combination to olefin molar ratio of at least about 2:1, whereby the resulting straight chain alkyl aryl compounds contain a relatively low proportion of the isomer wherein the aryl nucleus is attached at the two position of the alkyl chain.

2. In an alkylation process for producing straight chain alkylbenzenes using straight chain olefins, the improvement which comprises alkylating straight chain olefins containing from about 10 to 17 carbon atoms per molecule and averaging about 12 to 14 carbon atoms per molecule and containing not more than about 50% by weight of alpha olefins with benzene in the presence of an alkylation catalyst combination, of a Friedel-Crafts catalyst selected from the class consisting of activated aluminum chloride, activated aluminum bromide, and boron trifluoride, and an organo-nitro catalyst modifier, said alkylation conducted with a catalyst combination to olefin molar ratio of at least about 2:1, whereby straight chain

alkylbenzenes are produced with a relatively low 2-phenyl isomer content.

3. In an alkylation process for producing straight chain alkylbenzenes using straight chain olefins, the improvement which comprises alkylating straight chain olefins containing from about 10 to 17 carbon atoms per molecule and averaging about 12 to 14 carbon atoms per molecule and containing not more than about 50% by weight of alpha olefins with benzene in the presence of an alkylation catalyst combination of activated aluminum chloride and nitro methane, said alkylation conducted with a catalyst combination to olefin molar ratio of at least 2:1, whereby straight chain alkylbenzenes are produced with a relatively low 2-phenyl isomer content.

4. A process for producing straight chain alkyl aryl compounds containing a relatively low proportion of the isomer wherein the aryl nucleus is attached at the two position of the alkyl chain which comprises treating straight chain alpha olefins under catalytic conditions wherein said olefins are isomerized to olefins containing not more than about 50% by weight of alpha olefins and alkylating aromatic compounds with the resulting isomerized olefins in the presence of an alkylation catalyst combination of a Friedel-Crafts catalyst selected from the class consisting of activated aluminum chloride, activated aluminum bromide, and boron trifluoride, and organo-nitro catalyst modifier, said alkylation conducted with a catalyst combination to olefin molar ratio of at least about 2:1.

5. A process for producing straight chain alkylbenzenes which comprise treating straight chain alpha olefins containing from about 10 to 17 carbon atoms per molecule and averaging about 12 to 14 carbon atoms per molecule under catalytic conditions wherein said olefins are isomerized to olefins containing not more than about 50% by weight of alpha olefins and alkylating benzenes with the resulting isomerized olefins in the presence of an alkylation catalyst combination of a Friedel-Crafts catalyst selected from the class consisting of activated aluminum chloride, activated aluminum bromide, and boron trifluoride, and an organo-nitro catalyst modifier, said alkylation conducted with a catalyst combination to olefin molar ratio of at least about 2:1.

6. The process of claim 5 wherein said organo-nitro catalyst modifier is nitro methane.

7. The process of claim 5 wherein said organo-nitro catalyst modifier is nitrobenzene.

8. The process of claim 5 wherein said straight chain alpha olefins are isomerized in the liquid phase under catalytic conditions.

9. The process of claim 5 wherein said straight chain alpha olefins are isomerized in the vapor phase under catalytic conditions.

10. A process for producing straight chain alkylbenzenes which comprises treating straight chain alpha olefins containing from 10 to 17 carbon atoms per molecule and averaging about 12 to 14 carbon atoms per molecule under catalytic conditions wherein said olefins are isomerized to olefins containing not more than about 50% by weight of alpha olefins, and alkylating benzene with the resulting isomerized olefin in the presence of an alkylation catalyst combination of activated aluminum chloride and nitro methane, said alkylation conducted with a catalyst combination to olefin molar ratio of at least about 2:1.

11. The process of claim 3 wherein the molar ratio of said nitro methane to said aluminum chloride is from 1:1 to 5:1 and the molar ratio of said catalyst combination to olefin is from 2:1 to 10:1.

12. The process of claim 10 wherein the molar ratio of said nitro methane to said aluminum chloride is from

1:1 to 5:1 and the molar ratio of said catalyst combination to olefin is from 2:1 to 10:1.

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