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## ALKYL ISOMERIZATION OF NUCLEARLY ALKYL-SUBSTITUTED HYDROCARBONS

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This application is a continuation-in-part of my co-pending application Serial No. 358,987, filed June 1, 1953, now abandoned.

This invention relates to a process for converting tertiary alkyl-substituted aromatic hydrocarbons to their corresponding secondary alkyl-substituted isomers. More specifically, the invention concerns an isomerization process for reacting a tertiary alkyl-substituted aromatic hydrocarbon at isomerizing conditions with an isomerizing catalyst selected from a halide of aluminum or zirconium to thereby convert the tertiary alkyl substituent to a secondary alkyl group.

In certain processes and in the production of various compositions for specific uses, it is essential in many instances that the organic charging stock to the process or the compound employed in the composition be an alkyl-substituted aromatic compound in which the alkyl group has a secondary configuration; that is, the alkyl group is attached to the aromatic nucleus through a secondary carbon atom (defined as a carbon atom to which two other carbon atoms are attached). Thus, in the case of the long chain alkyl-substituted aromatic hydrocarbon sulfonates, useful as detergents and surface active agents, the compounds in which the alkyl substituent is attached to the aromatic nucleus through a secondary carbon atom are more effective detergents (that is, the sulfonate has a greater cleansing action or greater surface activity) and the resulting composition is generally less hygroscopic than sulfonates of the same molecular weight and composition in which the alkyl group is attached to the aromatic nucleus through a tertiary or a primary carbon atom. The secondary alkyl-substituted aromatic hydrocarbons are also more resistant to side reactions which occur during the sulfonation of an aromatic charging stock (that is, reactions such as dealylation, tar formation, etc. which are foreign to the desired sulfonation reaction); consequently, more powerful and effective sulfonating agents, the use of which is accompanied by low consumption and waste of reagents, may be employed in sulfonating secondary alkyl-substituted hydrocarbons than for sulfonating the corresponding primary and tertiary isomers. Similarly, in the case of certain oxidation inhibitors which may be synthesized from an alkyl aromatic hydrocarbon in a subsequent conversion reaction (as for example, in the production of certain alkyl-substituted p-phenylene diamine types of inhibitors) the isomers which contain a secondary alkyl substituent attached to one or more nitrogen atoms of the amino substituent have greater inhibitor potency and are generally more soluble in typical solvents than the corresponding tertiary and primary alkyl-substituted amines. Numerous other instances of preferred status of secondary alkyl aromatic hydrocarbons are known in the chemical arts and such preference is sufficiently established to indicate the utility of the present invention and its possible widespread application.

In one of its embodiments, the present invention relates to a process for producing a secondary alkyl-sub-

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stituted aromatic hydrocarbon which comprises subjecting a tertiary alkyl-substituted aromatic hydrocarbon having at least five carbon atoms in the tertiary alkyl substituent to the action of from about 0.1% to about 25% by weight of a metal halide selected from the group consisting of the chlorides and bromides of aluminum and zirconium at a temperature of from about 0° to about 75° C. to thereby convert said tertiary alkyl substituent to a secondary alkyl radical.

A more specific embodiment of the invention concerns a process for isomerizing a tertiary alkyl-substituted benzene hydrocarbon containing a tertiary alkyl group having from 9 to about 18 carbon atoms to the corresponding alkyl benzene hydrocarbon in which the long chain alkyl group is a secondary alkyl substituent which comprises contacting said long chain tert-alkyl benzene hydrocarbon with from about 0.1% to about 25% by weight of aluminum chloride at a temperature of from about 20° to about 60° C. and thereafter recovering from the reaction mixture said secondary alkyl-substituted benzene hydrocarbon.

In the alkylation of aromatic hydrocarbons, particularly mono-nuclear aromatic hydrocarbons of the benzene series, with olefin polymers to produce an alkylate product having an alkyl group containing the same number of carbon atoms as the alkylating agent utilized in the process, it is known that certain acidic alkylation catalysts, such as sulfuric acid, hydrofluoric acid, the ferric halides, anhydrous hydrogen fluoride and boron trifluoride, are capable of catalyzing the alkylation reaction to produce a greater yield of alkylate product than certain other acidic alkylation catalysts of the metal halide type. However, the alkylates thus produced have a structure corresponding to tertiary alkyl-substituted aromatic hydrocarbons in which the alkyl group is bound to the aromatic nucleus through a tertiary carbon atom (that is, a carbon atom having three of its bonds attached to other carbon atoms). It has now been discovered that the tertiary alkyl-substituted alkylates produced by the indicated alkylation catalyst may be converted to their secondary alkyl-substituted aromatic isomers, which in many instances, as aforesaid, form products of improved properties compared with the tertiary alkylates, by contacting the tertiary alkylate with a catalyst selected from the chlorides and bromides of aluminum and zirconium at isomerizing reaction conditions particularly adapted to effect the indicated isomerization. Thus, it becomes possible to take advantage of the greater yield of alkylate product formed by an alkylation reaction catalyzed with the aforementioned acidic alkylation catalyst which produces tertiary alkyl-substituted aromatic hydrocarbons and by isomerizing the product with the presently specified isomerization catalyst and at the particular reaction conditions suitable for the production of secondary alkyl-substituted aromatic hydrocarbons, the secondary alkylate may be produced with no substantial sacrifice in yield. By employing the indicated combination of alkylation and isomerization steps in a process in which the isomerization step follows the alkylation reaction, a yield of the secondary alkyl-substituted product may be obtained which corresponds with the yield of tertiary alkyl-substituted product, but the reduction in yield represented in the production of the secondary alkylate directly from the indicated isomerization catalyst in an alkylation reaction is eliminated.

The isomerization reaction of the present process is directed to charging stocks characterized as tertiary alkyl-substituted aromatic hydrocarbons in which the alkyl group contains at least five carbon atoms. The reaction is applicable to aromatic compounds having not only mono-cyclic, but also polycyclic structures, including ben-

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zene, naphthalene, anthracene or phenanthrene nuclei which may also contain other alkyl substituents of either primary, secondary or tertiary configuration. The process, however, is particularly applicable to the mono-nuclear or benzene hydrocarbons such as the alkylates of benzene itself, toluene, xylene, ethylbenzene, methylethylbenzene, cumene, mono-, or di-butyl benzene and homologues thereof. In the production of detergents, the benzene and toluene alkylates in which the alkyl substituent contains at least nine carbon atoms, generally up to about eighteen carbon atoms per alkyl group, and being further characterized in having only one of such long chain alkyl substituents on the benzene nucleus, constitute one of the preferred charging stocks herein, since the advantageous results realized in the application of the present process to such charging stocks are particularly evident in the improvement of the final product, as aforesaid. Thus, the alkylation products of benzene and toluene, formed by reacting the aromatic hydrocarbon with a long chain mono-olefin, such as a propylene tetramer fraction, utilizing concentrated sulfuric acid or substantially anhydrous hydrofluoric acid as a catalyst, is made up substantially in its entirety of tertiary-alkyl-substituted isomers. When such tertiary alkylates are subjected directly to sulfonation to form the corresponding tertiary alkyl benzene or toluene sulfonates, the product is a detergent which, although a highly effective material for detergent use in aqueous solutions, nevertheless, is somewhat hygroscopic when exposed to atmosphere containing appreciable amounts of water vapor. If, however, the tertiary alkyl-substituted alkylation product is subjected to an isomerization reaction of the character provided herein, the tertiary alkyl group is isomerized to a secondary alkyl group and if, thereafter, the resulting isomerized alkylate is converted to a detergent-type product by sulfonation, the resulting secondary alkyl aromatic sulfonate is not only a more effective detergent in that its surface activity is enhanced, but the product is substantially less hygroscopic and, therefore, resists caking when exposed to humid atmospheres than the corresponding sulfonate of the tertiary alkylate. The present isomerization process is, therefore, particularly applicable to benzene and toluene alkylates containing long chain alkyl groups which are substituted on the aromatic nucleus by virtue of a prior alkylation reaction effected in the presence of an acid-acting catalyst which results in the substitution of a tertiary alkyl group on the aromatic nucleus.

The tertiary alkyl isomerization process of this invention is effected catalytically in the presence of a metal halide selected from the group consisting of the aluminum and zirconium chlorides and bromides, the catalyst being supplied to the isomerization reactor in a substantially anhydrous condition and preferably in the presence of the hydrogen halide corresponding to the metal halide utilized as catalyst in the reaction. The catalyst is supplied to the reaction zone in an amount corresponding to at least 0.1% and preferably from about 5 to about 25% by weight of the tertiary alkyl aromatic hydrocarbon charged to the process, the amount of metal halide supplied to the reaction zone in any event being sufficient to convert the charge stock to the secondary alkyl-substituted aromatic hydrocarbon. The actual amount of catalyst required in any particular conversion depends upon such factors as the activity of the catalyst, the ease of isomerization, the stability of the aromatic reactant in the presence of the catalyst, and upon other factors mutually operable in the process. The catalyst is preferably introduced into the reaction mixture in a finely divided condition, accompanied by stirring of the reaction mixture to disperse the catalyst throughout the reaction zone or, alternatively, the catalyst may be dissolved in a suitable solvent therefor, prior to charging the same into the reaction zone. The hydrogen halide, if utilized during the conversion, is introduced into the reaction mixture as the anhydrous gas below the surface of the reac-

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tion mixture containing the catalyst. The reaction is desirably operated at a superatmospheric pressure, sufficient to maintain the organic portion of the charge stock in substantially liquid phase condition, although pressures in excess of about 50 pounds per square inch are generally not required within the temperature range specified for the reaction, which may suitably be from about 0° to about 75° C. and preferably from about 20° to about 60° C., depending upon the ease of conversion and the stability of the charge stock.

Aluminum and zirconium chlorides and bromides are unique among the various types of acid-acting catalysts, which includes, among others, such reagents as sulfuric acid, hydrogen fluoride, the zinc halides and ferric halides, etc., in that the chlorides and bromides of aluminum and zirconium effect isomerization of tertiary alkyl groups to their corresponding secondary alkyl isomers, whereas other acid-acting catalysts of the aforementioned type are either ineffective in causing any transformation of the alkyl substituent on the aromatic hydrocarbon nucleus from tertiary to secondary alkyl structure, or tend to promote isomerization in the opposite direction; that is, from primary and secondary alkyl configuration to tertiary alkyl configuration.

The yield and the desired direction of the isomerization reaction are enhanced by the presence in the reaction zone of a suitable diluent of the reaction mixture during the contact of the selected metal halide with the alkyl aromatic charge stock. Suitable diluents for this purpose which tend to reduce dealkylation of the aromatic compound, condensation thereof into tarry materials (particularly in the case of the phenols and long chain alkyl-substituted aromatic hydrocarbons) and other undesirable side reactions, include particularly the relatively inert, straight chain paraffinic or naphthenic hydrocarbons such as n-pentane, cyclohexane, n-hexane, n-heptane, etc. In certain cases, aromatic hydrocarbons, such as benzene, toluene, naphthalene, etc., may be utilized as reaction diluents, as for example, when the reaction is effected at temperatures which result in the transfer of alkyl groups to the aromatic nucleus of the hydrocarbon utilized as diluent. Particularly preferred diluents for the reaction are the compounds which represent the charge stock free of isomerizable tertiary alkyl groups, such that any alkyl groups which split from the charge stock during the isomerization reaction are transferred directly to the diluent in the presence of the aluminum halide catalyst which also acts in the capacity of an alkylation catalyst in such modification of the process. Thus, the use of benzene as a diluent in the isomerization of a tertiary-alkyl benzene or a di-tertiary-alkyl benzene forms the secondary-alkyl benzene from any secondary-alkyl group split from the charge stock during the isomerization reaction. The diluent is preferably charged into the isomerization reaction mixture in an amount at least equal in volume to the tertiary-alkyl-substituted aromatic compound subjected to isomerization, preferably in an amount of from about 0.5 to about 6 moles per mole of the latter charge stock.

Following the completion of the isomerization reaction, generally within a reaction period of from about 10 minutes to about 6 hours, the spent metal halide catalyst (aluminum or zirconium halide) which forms a sludge-like phase in the reaction mixture during the course of the isomerization may be recovered from the reaction mixture, either by separation of the sludge therefrom (for example, by decantation or by washing the reaction mixture with a stream of water which may contain a basic neutralizing agent, such as sodium hydroxide) or the product, unconverted charge stock and/or diluent may be distilled from the reaction mixture. Alternatively, the metal halide sludge may be separated from the reaction mixture and utilized, at least in part, as the catalyst charge to a succeeding isomerization reaction. In the latter type of reaction, additional fresh metal halide

is preferably added to the sludge prior to contacting the additional charge of alkyl aromatic compound therewith for isomerization. The isomerized conversion product may be separated from the remaining components of the reaction mixture by any suitable means; as for example, by distillation. The separated solvent and any unconverted portions of the charge stock may be recycled, if desired, in the process.

The several specific embodiments of the present invention and the specific means for effecting the present isomerization are further illustrated in the following examples, which, however, are not intended to limit the generally broad scope of the invention necessarily in accordance therewith, but are for illustrative purposes only.

#### EXAMPLE I

p-Dodecyltoluene, which by infra-red analysis was determined to be 98% by weight of the tertiary-dodecyl isomers, was prepared in a preliminary procedure by alkylation of toluene with dodecylene (the  $C_{12}$  or tetramer fraction of a propylene polymerization product) in the presence of 98.5% sulfuric acid catalyst and at a temperature of from about 30° to about 50° C., the alkylate product being separated from the resulting hydrocarbon layer formed in the alkylation reaction by distillation of the 275°-325° C. fraction therefrom. The tertiary-dodecyltoluene feed stock was charged into a stirred reaction vessel with various amounts of anhydrous aluminum chloride isomerization catalyst, with and without added diluent (indicated in the following Table I) and the reaction mixture thereafter heated at the indicated temperature for 1.5 hours. The reaction mixture was thereafter washed with 5 volumes of water to remove aluminum chloride and the recovered organic product dried and distilled to remove solvent (if any) therefrom. The following Table I indicates the results obtained by such conversion:

Table I

ISOMERIZATION OF TERTIARY-DODECYLTOLUENE IN THE PRESENCE OF ALUMINUM CHLORIDE

Charge Stocks, gms.:						
p-Tertiary-Dodecyltoluene.....	100	100	262	100	100	100
Aluminum Chloride.....	10	2	26	10	10	10
Reaction Conditions:						
Temperature, ° C.....	30	30	30	0	65	75
Contact time, Hrs.....	1.5	1.5	1.5	1.5	1.5	1.5
Product:						
Loss to Catalyst Sludge, Wt.						
Percent of Charge.....	11	0.2	8.7	1.5	21	23
Loss to Dealkylation, Vol. Percent of Charge.....	34	10	27	15	28	29
Properties of 275°-325° C. Product *:						
$N_D^{20}$ .....	1.4909	1.4900	1.4923	1.4909	1.4961	1.4960
Dispersion, @ 20° C.....	118.0	117.7	118.1	118.0	118	118
Bromine No.....	0.1	0.2	0.1			
Ratio of sec./tert. Dodecyltoluene in Product.....	40/60	10/90	40/60	40/60	40/60	40/60

\*NOTE.—Tertiary-dodecyltoluene charging stock has a refractive index,  $N_D^{20}$ , of 1.4907 a dispersion, @ 20° C., of 116.8 and a bromine No. of 1.0.

#### EXAMPLE II

A solution of one molar proportion each of benzene and 2,3-dimethyl-2-phenylbutane (a tertiary-hexylbenzene) was introduced into a stirred alkylation reactor and adjusted to a temperature of 30° C. To the resulting mixture, as the latter was stirred, was added 0.37 molar proportion (30% by weight of the tertiary-hexylbenzene) of anhydrous aluminum chloride dissolved in one molar proportion of benzene. The mixture was continuously stirred for 4 hours at the above temperature, followed by washing the mixture with water to remove catalyst, drying the hydrocarbon product and subjecting the product to analysis. Infra-red analysis indicated that 100% of the product recovered (70% theoretical) was 2,2-dimethyl-3-phenylbutane (a secondary-hexylbenzene). It will be noted that alkylation and isomerization occur in a single one-step conversion reaction, resulting in the

formation of the secondary-hexylbenzene product from a tertiary alkylating agent.

#### EXAMPLE III

A solution of 2 molar proportions of benzene and 1 molar proportion of p-di-(2,3-dimethyl-2-butyl)-benzene (a di-tertiary-hexylbenzene) was added to a solution of 2 molar proportions of benzene which contained in solution 20% by weight of the di-tertiary-hexylbenzene of anhydrous aluminum chloride, the solution also being saturated with dry hydrogen chloride gas before mixing with the hexylbenzene-benzene solution. It is thus evident that the resulting reaction mixture contains a total molar ratio of benzene to tertiary-hexylbenzene of 4 to 1. The mixture was stirred for 4 hours at 30° C., thereafter washed with water, dried, and fractionally distilled. A product yield of 52% of theoretical, 98% of which was mono-secondary-hexylbenzene, was recovered, none of the di-tertiary-hexylbenzene remaining unconverted.

In a similar experiment, utilizing the same charging stocks in the same molar proportions, except that anhydrous ferric chloride in an amount representing 20% by weight of the p-di-tertiary-hexylbenzene was charged to the reaction in the form of a benzene solution thereof, 95% of the product recovered (41% of theoretical based upon the hexylbenzene charged) was mono-tertiary-hexylbenzene and the product contained no detectable quantity of secondary-hexylbenzene.

The product formed by alkylating benzene with 1-chloro-3,3-dimethylbutane (an alkylating agent which produces a tertiary alkyl substituent) or with 1-chloro-, or 2-chloro-2,3-dimethylbutane in the presence of anhydrous aluminum chloride and hydrogen chloride gas was consistently 2,2-dimethyl-3-phenylbutane (a secondary-alkylbenzene) whereas the product formed by alkylating benzene with the above tertiary-alkyl alkylating agents in the presence of sulfuric acid, anhydrous hydrogen fluoride

and ferric chloride was 2,3-dimethyl-2-phenylbutane, (a tertiary-alkyl benzene).

#### EXAMPLE IV

In a series of experiments conducted at various temperatures it was found that the most effective range of temperatures was from about 20° to about 60° C., although temperatures of from about 0° to about 75° C. also resulted in yields of product (sec-alkyl-substituted aromatic hydrocarbon) sufficient to represent an operable process. Thus, utilizing a mixture of p-tert-dodecyltoluene isomers as a typical charge stock and anhydrous aluminum chloride (dissolved in about 10 volumes of benzene) as a catalyst, of the dodecyltoluenes recovered, 55% was the secondary isomer when the conversion was effected at a temperature of 0° C., 75% of the dodecyltoluene product was the secondary isomer at a conversion temperature of 20° C., 95% was the secondary isomer at 50° C. and

95-98% was the secondary isomer at 65° and 75° C., although a larger proportion of the charge stock is converted to side reaction products (i. e., alkyl benzenes and alkyl toluenes other than the dodecyltoluene charged) as the reaction temperature is increased. Above about 75° C., the conversion to side-reaction products becomes too excessive to be considered a practical process.

In other experiments utilizing the same reactants except that zirconium chloride was substituted for aluminum chloride as catalyst, less conversion of the charge stock to side reaction products is obtained at the same temperatures at which aluminum chloride is employed, but the proportion of recovered alkylate converted to the secondary isomer is less than for the aluminum chloride catalyzed reaction at the same temperature. In general, higher reaction temperatures are required for the conversion of the same charge stock in the presence of zirconium halide catalysts than in the case of aluminum halide catalysts.

I claim as my invention:

1. A process for producing a secondary alkyl-substituted aromatic hydrocarbon which comprises subjecting a tertiary alkyl-substituted aromatic hydrocarbon having at least 5 carbon atoms in the tertiary alkyl substituent to the action of from about 0.1% to about 25% by weight of a metal halide selected from the group consisting of the chlorides and bromides of aluminum and zirconium at a temperature of from about 0° to about 75° C. to thereby convert said tertiary alkyl substituent to a secondary alkyl radical.

2. The process of claim 1 further characterized in that said aromatic hydrocarbon is monocyclic.

3. The process of claim 1 further characterized in that said aromatic hydrocarbon is a toluene hydrocarbon.

4. The process of claim 3 further characterized in that said tertiary alkyl substituent is in the para position.

5. The process of claim 1 further characterized in that said temperature is from about 20° to about 60° C.

6. The process of claim 1 further characterized in that the conversion of said tertiary alkyl-substituted aromatic hydrocarbon is effected in the presence of an inert diluent of the reaction mixture.

7. The process of claim 6 further characterized in that said diluent is benzene.

8. The process of claim 7 further characterized in that

said tertiary alkyl-substituted aromatic hydrocarbon is a di-tertiary alkyl-substituted compound.

9. The process of claim 6 further characterized in that said diluent is a paraffinic hydrocarbon boiling at a temperature below the boiling point of said aromatic hydrocarbon.

10. The process of claim 1 further characterized in that the reaction is effected in the presence of a hydrogen halide, the halogen of which corresponds to the halogen of said metal halide.

11. A process for isomerizing a tertiary alkyl-substituted benzene hydrocarbon containing a tertiary alkyl group having from 9 to about 18 carbon atoms to thereby form the corresponding alkyl benzene hydrocarbon in which said tertiary alkyl group is converted to a secondary alkyl substituent which comprises contacting said tertiary alkyl benzene hydrocarbon with from about 0.1% to about 25% by weight of a metal halide selected from the group consisting of the chlorides and bromides of aluminum and zirconium at a temperature of from about 20° to about 60° C. and thereafter recovering from the reaction mixture an alkyl-substituted benzene hydrocarbon in which the alkyl group contains from 9 to about 18 carbon atoms and wherein the alkyl substituent is attached to the benzene nucleus through a secondary carbon atom.

12. The process of claim 11 further characterized in that said benzene hydrocarbon comprises dodecylbenzene.

13. The process of claim 11 further characterized in that said alkyl benzene hydrocarbon comprises alkyl toluene.

14. The process of claim 11 further characterized in that said process is effected in the presence of a diluent for the reaction consisting of benzene.

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