

1

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**ALKYLATION OF AROMATIC HYDROCARBONS**  
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No Drawing. Continuation-in-part of application Ser. No. 368,397, May 18, 1964, which is a continuation-in-part of application Ser. No. 348,278, Feb. 28, 1964. This application Mar. 21, 1968, Ser. No. 714,815

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12 Claims

### ABSTRACT OF THE DISCLOSURE

Process for producing n-alkyl aromatic hydrocarbons having an increased center substitution of the aromatic nucleus on the n-alkane wherein toluene, benzene or xylene is alkylated with an n-alkyl chloride having 9–16 carbon atoms per molecule in the presence of a Friedel-Crafts catalyst at a temperature between  $-25^{\circ}$  C. and  $10^{\circ}$  C. for 5–60 minutes and thereafter the reaction mixture is raised to a temperature of  $30^{\circ}$ – $100^{\circ}$  C. and maintained at this temperature for a least 4 minutes. The product is a valuable precursor for making detergents.

This application is a continuation-in-part of application Ser. No. 368,397, filed May 18, 1964, which is a continuation-in-part of application Ser. No. 348,278, filed Feb. 28, 1964, and now abandoned.

This invention relates to an improved method for alkylating hydrocarbons, and more particularly relates to a method of alkylating aromatic hydrocarbons to form n-alkyl aromatic hydrocarbons, and the sulfonic acids and salt thereof.

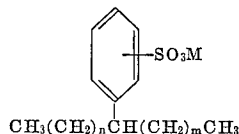
The method of this invention relates particularly to the production of n-alkyl hydrocarbons, particularly n-alkyl benzene hydrocarbons which are subsequently sulfonated to form n-alkyl benzene sulfonic acids, the latter when neutralized with an alkali, such as caustic soda, produce well known types of biodegradable wetting agents, surfactants, and detergents, namely sodium n-alkyl benzene sulfonates.

Early production of sodium n-alkyl aryl sulfonates utilized an alkyl hydrocarbon fraction derived from a petroleum hydrocarbon distillate having a boiling range within the kerosene range. This hydrocarbon fraction was chlorinated and the resultant alkyl chloride condensed with benzene, toluene, xylene, or the like in the presence of a Friedel-Crafts catalyst, such as anhydrous aluminum chloride. When such alkyl fraction is chlorinated, and the chlorides condensed with benzene, the resulting alkyl aromatic hydrocarbon compounds have become known as "keryl benzenes."

Subsequently, benzene and propylene tetramer have been used as starting materials in the preparation of dodecylbenzene which is subsequently processed to form dodecylbenzene sulfonate. While it is known that the alkyl benzene sulfonates are useful detergents, it has been only recently recognized that the foregoing materials are not degraded by sewage flora or microorganisms, and therefore accumulate in ground waters. This problem is particularly enhanced when the alkyl group is branched, as for example, in the sodium tetrapropylene benzene sulfonates. Consequently, industry has turned its attention

2

to the manufacture of straight chain benzene sulfonates which can be represented by the formula:



wherein M is alkali metal (or quaternary nitrogen cation), typically sodium and  $m$  and  $n$  are integers such that

$$6 \leq m+n \leq 14$$

It is known that the n-alkyl benzene sulfonates which are most biodegradable are those with the phenyl group positioned near the end of the alkyl chain ( $n/m \ll 1$ ). However, such materials are poor detergents. For example, sodium 1-tridecylbenzene sulfonate is almost wholly water insoluble although it may be made soluble by mixing it with other alkyl benzene sulfonates which have the phenyl group positioned along the alkyl chain. Thus, the most efficient detergents have the phenyl group positioned near the middle of the alkyl chain ( $n/m \sim 1$ ). Manufacturers of synthetic detergents, in seeking an optimum compromise product, have consequently suggested that no more than 25% of the alkylate have the phenyl group substituted on the 2-carbon atom, with 50% substituted on the 2-, and 3-carbon atoms.

Furthermore, with reference to the above formula, a mixture of homologues not only having different values of  $m$  and  $n$  but also different values of  $m+n$  give the most desirable detergent. A suitable distribution of homologues of n-alkyl benzenes useful for the manufacturer of detergents is illustrated in Table 1, below.

TABLE 1

Typical homologues, distribution of alkyl benzenes, $m+n$ :	Percent
$\leq 7$ -----	2
8 -----	10
9 -----	20
10 -----	40
11 -----	25
$> 11$ -----	3

As hereinbefore stated, the isomers with the aryl group near the end of the chain ( $n/m \ll 1$ ) are readily biodegradable, while the isomers with the aryl group nearest the middle of the chain ( $n/m \sim 1$ ) result in detergents having the best washing action. It is evident that for every  $m+n$  there is an optimum distribution of  $n/m$ . In the past it has been found that under all known conditions  $n/m$  has been too small. In particular, the content of 1-, and 2-aryl, n-alkanes has been to large.

It is an object of this invention to provide a method of obtaining an optimum distribution of  $n/m$  isomers of n-alkyl aromatic hydrocarbons having any  $m+n$  distribution.

A further object of this invention is to provide a novel method of alkylating an aromatic hydrocarbon which gives rise to smaller concentration of 1-, and 2-aryl n-alkyl compounds.

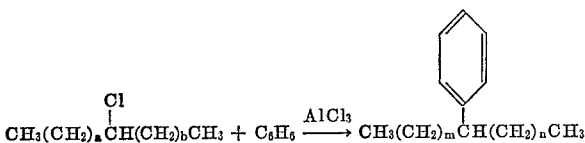
A still further object of this invention is to provide a novel method of alkylating an aromatic hydrocarbon where there is an increase in the concentration of n-alkyl aromatic hydrocarbon having substitution near the center

of the chain and a substantial reduction in branched chain alkyl aryl compounds.

Another object of this invention is to provide a novel method of forming n-alkyl benzenes whose sulfonates possess excellent detergent properties and are capable of being degraded by micro-organisms.

Still another object of this invention is to increase the yield of those n-alkyl benzene isomers which are useful detergents by reducing the formation of 1-, and 2-phenyl n-alkyl isomers.

One method of making long chain normal n-alkyl aromatic hydrocarbons is by the Friedel-Crafts reaction of an aromatic hydrocarbon such as benzene with n-alkyl chlorides as illustrated by the following equation:



wherein  $a$  and  $b$  are integers, such that  $a+b=m+n$ .

The n-alkyl chloride can be made by chlorinating an n-paraffin mixture having a desired distribution of molecular weights. Although the isomeric distribution of  $a/b$  is more or less randomly determined by chlorination, we have found that the isomeric distribution of the alkyl benzene ( $m/n$ ) is not determined solely by the isomeric distribution of the chloride ( $a/b$ ). In fact, the isomeric distribution of the alkyl benzenes formed under normal alkylation conditions is apparently insensitive to the isomeric distribution of the alkyl chloride so that even when starting with a single alkyl chloride an isomeric mixture of alkyl benzenes results, and it is similar to the isomeric distribution obtained from a chlorinated n-paraffin. The isomeric distribution of the n-alkyl benzenes obtained by effecting the alkylation of benzene at normal alkylation conditions is not effected by changing the solvent, varying the concentration of alkyl chloride relative to the aromatic hydrocarbon, or varying catalyst concentrations.

In accordance with our co-pending application Ser. No. 348,278, we found that the isomeric distribution of n-alkyl aromatic hydrocarbons were favorably altered by effecting alkylation at a temperature of from about  $-25^\circ$  to  $10^\circ$  C., i.e., there was greater center substitution of the phenyl group on the n-alkyl hydrocarbon. We have now found that the isomeric distribution of the n-alkyl aromatic hydrocarbon may still further be more favorably improved by rapidly raising the temperature of the reaction mixture to a temperature of from about  $30^\circ$  to about  $100^\circ$  C., after partially alkylating the n-alkyl hydrocarbon at temperatures of from about  $-25^\circ$  to  $10^\circ$  C. As set forth in our aforementioned application, in order to effect alkylation of the n-alkyl chlorides within such a low temperature range, it is necessary that the concentration ratio of aryl compounds, n-alkyl chlorides and paraffin be selected so the mixture is fluid (i.e., not over 50% frozen). The catalyst may be aluminum chloride. A solvent may be used to assist in achieving the low temperatures necessary for liquid phase alkylation. Such solvents include n-kerosene, carbon disulfide, pentane, and liquid sulfur dioxide with n-kerosene being particularly effective where n-alkyl chlorides are the alkylating hydrocarbons. The preferred aromatic hydrocarbons are selected from the group consisting of benzene, toluene and xylene.

We have now found that the reactivity of 1-chloro alkane during alkylation is substantially less than the other chloro alkanes at such low temperatures, and accordingly, a large percentage of the 1-chloro alkane is passed to the subsequent sulfonation reaction. However, by subsequently rapidly heating the reaction mixture to a temperature of from about  $30^\circ$  to about  $100^\circ$  C., preferably  $60^\circ$  C., and maintaining the reaction mixture at such temperature for from 4 to 40 minutes, 1-chloro alkanes in the reaction mixture react with the benzene to form

phenyl alkanes with the phenyl group distributed towards the middle of the chain. Thus, the resulting compounds are superior in detergent action to the material which would be produced were the 1-chlorine replaced directly with a phenyl group.

In accordance with a preferred embodiment of our invention, a mixture of n-paraffins is first chlorinated to form n-alkyl chlorides, as for example, described in our co-pending application Ser. No. 348,278, filed Feb. 28, 1964. The mixture of n-paraffins is derived from a petroleum distillate fraction boiling in the kerosene range, with the n-paraffins having from 9 to 16 carbon atoms per molecule, preferably 11 to 14. It is desirable to only partially chlorinate the mixture so as to minimize the formation of polychlorides.

The resulting n-alkyl chlorides in admixture with unreacted n-paraffins are then introduced into a reaction zone. An aromatic hydrocarbon, such as benzene, is introduced into the reaction zone in an amount of from about 1 to 25 moles of the aromatic hydrocarbon per mole of n-alkyl chlorides, preferably of from 5 to 20 moles. A Friedel-Crafts catalyst, such as aluminum chloride, is added to the mixture, and the mixture maintained at a temperature of from about  $-25^\circ$  C. to  $10^\circ$  C., but above the temperature at which 50% of the mixture is a solid. The reaction mixture is maintained under such conditions for from 5 to 60 minutes, preferably in a batch reaction for a time sufficient for the reaction rate to drop to about 10% of the initial reaction rate. In a continuous reactor, the residence time is adjusted so that from 75 to 95% of the n-alkyl chlorides are converted, preferably from 85 to 90%.

The reaction mixture is then heated to a temperature of from about  $30^\circ$  to about  $100^\circ$  C., preferably  $60^\circ$  C., and maintained at such temperature for from 4 to 40 minutes. Preferably, the temperature is rapidly raised to the higher temperature range thereby to improve center substitution of the unreacted n-alkyl chlorides.

The products from the alkylation zone are thereafter isolated, such as by distillation; and sulfonated in a manner well known to those skilled in the art, such as by contacting the distilled n-alkyl benzenes with oleum to form n-alkyl benzene sulfonic acids, which are then neutralized with an aqueous sodium hydroxide solution to form sodium n-alkyl benzene sulfonates having more center substituted n-alkanes and less branched chain sulfonates than heretofore obtained.

#### EXAMPLE I

As an example of our invention, a normal paraffin having a composition as shown in Table 2, was chlorinated on a steam bath until it had gained about 2.5% in weight. The mixture contained 80 grams of alkyl chlorides and 220 grams of the unreacted paraffins.

Table 2.—Composition of normal paraffin mixtures

	Percent
C <sub>12</sub> -----	24
C <sub>13</sub> -----	45
C <sub>14</sub> -----	31

To the reaction mixture was added, 150 grams of benzene and 6 grams of aluminum chloride. The reaction mixture was maintained at a temperature of  $-17.5^\circ$  C. for 24 minutes, after which, the reaction mixture was rapidly raised to a temperature of  $60^\circ$  C. and maintained at such temperature for 25 minutes. Thereafter, the product was hydrolyzed, distilled and analyzed, with the analysis being set forth as Experiment A in Table 3 below. Also set forth in Table 3, as Experiment B, is the analysis of a product obtained by effecting the alkylation of a similar mixture of n-alkyl chloride at a temperature of  $65^\circ$  C. Experiment C set forth the analysis of the

product obtained when alkylation is effected solely at the low temperature without post heat treatment.

TABLE 3

Isomer	Experiment		
	A, mol percent	B, mol percent	C, mol percent
2 $\phi$ -----	20	27	23
3 $\phi$ -----	18	18	18
4 $\phi$ -----	17	16	16
5 $\phi$ -----	19	17	19
6, 7 $\phi$ -----	25	19	23
Branched chain-----	1	3	1

## EXAMPLE II

A mixture of straight chain hydrocarbons in the C<sub>9</sub>-C<sub>15</sub> range was chlorinated at -10° C. in the presence of soft ultra violet light until about 5% organically bound chlorine was present.

The chlorinated mixture is alkylated using an aluminum chloride catalyst and about 10 moles of benzene/mole of organic chloride at -25° C. for about 20 minutes followed by heating to 60° C. in the presence of the catalyst for 10 minutes. The 2-phenylalkane content was 17.6%.

While we have described that alkylation of the aromatic hydrocarbons is effected in the presence of aluminum chloride, other catalysts are contemplated. Accordingly, as set forth in the appended claims, Friedel-Crafts catalysts are to be interpreted as a metallic halide type Lewis acid, wherein the metallic halide includes aluminum halides, boron halides, and ferric halides.

Although the present invention has been described and illustrated with reference to specific examples, it is understood that modifications and variations may be made by those skilled in the art within the principles and scope of the invention as expressed in the appended claims.

What is claimed is:

1. In the production of n-alkyl aromatic hydrocarbons, a process for increasing center substitution of the aromatic nucleus on the n-alkane comprising:

(a) contacting an aromatic hydrocarbon selected from the group consisting of toluene, benzene and xylene with an n-alkyl chloride having from 9 to 16 carbon atoms per molecule in the presence of a Friedel-Crafts catalyst at a temperature between about -25° C. and about 10° C. for between about 5 and 60 minutes; and

(b) thereafter raising the reaction mixture to a temperature of from about 30° C. to about 100° C., the reaction mixture being maintained at a temperature between about 30° C. and about 100° C. for at least about 4 minutes.

2. The process defined in claim 1 wherein the aromatic hydrocarbon is benzene.

3. The process defined in claim 2 wherein said reaction mixture is maintained at a temperature within said higher temperature range for from 4 to 40 minutes.

4. The process defined in claim 2 wherein said reaction mixture is rapidly raised to the temperature of step (b).

5. The process defined in claim 2 wherein the mole

ratio of aromatic hydrocarbon to n-alkyl chlorides is from 1:1 to 25:1.

6. The process defined in claim 2 wherein the Friedel-Crafts catalyst is aluminum chloride.

7. The process of claim 2 wherein the alkylation is effected in the presence of liquid sulfur dioxide as a solvent.

8. In the production of n-alkyl aromatic hydrocarbons, a process for increasing center substitution of the aromatic nucleus on the n-alkane comprising:

(a) contacting an aromatic hydrocarbon selected from the group consisting of toluene, benzene and xylene with an n-alkyl chloride having from 9 to 16 carbon atoms per molecule in the presence of a Friedel-Crafts catalyst at a temperature between about -25° C. and about 10° C. until 75 to 95% of the n-alkyl chlorides are converted; and

(b) thereafter raising the reaction mixture to a temperature of from about 30° C. to about 100° C., the reaction mixture being maintained at a temperature between about 30° C. and about 100° C. for at least 4 minutes.

9. The process defined in claim 8 wherein the aromatic hydrocarbon is benzene, the catalyst is aluminum chloride and the reaction mixture is rapidly raised to the temperature of step (b).

10. The process defined in claim 9 wherein the mole ratio of aromatic hydrocarbons to n-alkyl chlorides is from 1:1 to 25:1.

11. In the production of n-alkyl aromatic hydrocarbons, a process for increasing center substitution of the aromatic nucleus on the n-alkane comprising:

(a) contacting an aromatic hydrocarbon selected from the group consisting of toluene, benzene and xylene with a n-alkyl chloride having from 9 to 16 carbon atoms per molecule in the presence of a Friedel-Crafts catalyst at a temperature between about -25° C. and about 10° C. until the reaction rate is about 10% of the initial reaction rate; and

(b) thereafter raising the reaction mixture to a temperature of from about 30° C. to about 100° C., the reaction mixture being maintained at a temperature between about 30° C. and about 100° C. for at least about 4 minutes.

12. The process defined in claim 11 wherein the aromatic hydrocarbon is benzene, the catalyst is aluminum chloride and the reaction mixture is rapidly raised to the temperature of step (b).

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U.S. Cl. X.R.

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