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PROCESS FOR THE PREPARATION OF DETERGENT ALKYLATE

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ABSTRACT OF THE DISCLOSURE

An n-alkyl benzene detergent alkylate composition having a desirably high content of internally substituted phenyl alkanes is produced by alkylating benzene with a partially chlorinated detergent-range n-paraffin or mixture thereof in the presence of a recycle stream recovered as a fraction from a previous alkylation run, said fraction being rich in the external phenyl alkane isomers of the highest molecular weight alkyl benzenes present in the run from whence obtained.

This invention relates to a process for the preparation of detergent alkylate and more particularly concerns the production of an isomeric mixture of detergent grade monophenyl-n-alkane wherein the presence of internal isomers predominates. In accordance with the preferred embodiment of this invention, a method is provided for alkylating benzene with an n-alkyl halide or straight-chain olefin in the presence of a recycle product stream having a rich content of the external isomers of a detergent grade monophenyl n-alkane whereby said isomer content equilibrates to an isomeric distribution corresponding to that obtained in the underlying alkylation reaction.

The present invention is directed to the process for preparing alkyl benzenes wherein the alkyl substituents are derived from a detergent grade linear paraffin or mixture thereof. Such paraffins vary in carbon atom length from about 10–15. Two related ways are currently favored by the industry for producing n-alkyl benzenes. Each of these process schemes initially contemplates partially chlorinating a detergent grade paraffin or mixture thereof to yield a chlorinated product having a high selectivity to monochlorides. The partially chlorinated product itself can be used to alkylate benzene in accordance with the Friedel-Crafts reaction or alternately, the product can be dehydrochlorinated to yield an olefinic alkylating agent. Either process variant results in the same general type of alkylate product. As is well known, the sulfonate salts of these alkylates are colloidally soluble surfactants. Additionally, these surfactants are biodegradable for which reason they are presently of considerable commercial interest.

In order to point up the usefulness of our invention, it would be desirable to consider briefly the chemical make-up of the detergent alkylates prepared in the foregoing manner. Upon partially chlorinating a linear paraffin, one obtains a near-statistical distribution of alkyl monochlorides composed of all possible isomers. This distribution is not materially altered even upon dehydrochlorinating the product in accordance with the conventional dehydrohalogenation practices. In the course of alkylating benzene with either the partially chlorinated product or dehydrohalogenated derivative thereof, there is obtained an alkylate product composed of all the secondary isomers of the alkyl benzene. Essentially no primary alkyl benzenes are formed since the primary chlorides or alpha olefins present in the alkylating agent isomerize to the secondary form during the alkylation reaction. Thus, as mentioned, the resulting alkylate is an isomeric alkyl benzene mixture having an equilibrium distribution of all possible secondary isomers.

It has been found that the various isomers of a given species of alkyl benzene provide surfactants having different detergency properties. The term detergency properties not only refers to the actual detersive ability of the surfactant but also contemplates other related properties of importance such as foam stability, wetting power and the like. Generally, the detergency properties of any given species of alkyl benzene improves as the phenyl attachment moves toward the center of the alkane chain. The differences noted are of such magnitude that the sulfonate salts of the external secondary isomers of a detergent grade n-alkyl benzene are regarded to be comparatively inferior detergents. What constitutes an external isomer depends to a large measure upon the particular alkyl benzene concerned. In the case of n-decylbenzene, n-hendecylbenzene and n-dodecylbenzene, the term external secondary isomers contemplates the 2- and 3-phenyl isomers; whereas, this term additionally contemplates the 4-phenyl isomer where the alkylate is either n-tridecylbenzene, n-tetradecylbenzene or n-pentadecylbenzene. Since the boiling point of the various secondary alkyl benzene isomers increases as the phenyl attachment moves toward the terminal portion of the alkane chain, it is possible to recover the bulk of the internal isomers of any particular alkyl benzene by careful distillation practices.

In our initial efforts directed toward upgrading the external isomers of an n-alkylbenzene, we found that pure samples of these isomers could be readily isomerized to yield the normal isomeric distribution upon heating in the presence of a catalytic amount of aluminum chloride. The logical extension of this finding was to recycle the external isomers recovered from an alkylation operation. When this was attempted, however, disappointing results were obtained in that the recycled external isomers failed to isomerize with any degree of consistency.

After considerable experimental investigation, it was found that isomerization catalyst poisoners are generated in the type of alkylation reaction environment with which this invention is concerned and moreover, that these poisoners are prone to become entrained in the fraction recovered for purpose of recycle. While we have been unable to characterize completely these impurities, it appears that they are some type of condensed or fused ring aromatic compounds. It further was noted that these compounds are such potent inhibitors that amounts thereof even in the order of 1% or even lower will effectively inhibit the isomerization of the external isomers present in the recycle fraction under the conditions normally experienced in the alkylation operation. Efforts to rid contaminated recycle fractions of these impurities by treatment with agents known to have the ability for preferentially absorbing polynuclear aromatic compounds were of no avail. The key to obtaining satisfactory recycle streams was found to hinge upon observing proper distillation practices in recovering said streams and the implementation of this finding constitutes the concept behind this invention.

In order to facilitate an understanding of the manner of practicing the instant invention, it warrants reverting to a discussion of the chemical nature of the alkylation reaction mixtures herein concerned. As previously mentioned, the alkylating agent contemplated is either a partially chlorinated paraffin or mixture thereof or an olefinic material derived therefrom. In preparing such chlorinated products it is not possible to produce monochlorides exclusively as the formation of a minor amount of dichlorides is inherent in the process. The amount of dichlorides formed will vary proportionally to the level of chlorination observed. For example, at a 10% mole level of chlorination about 95% of the total chlorides produced will be monochlorides and at a 40% mole level the monochloride content decreases to about 80% of the amount of chlorides formed.

When benzene is alkylated with these partially chlorinated products, part of the dichlorides react with benzene to form alicyclic compounds. The alicyclic compounds produced are believed to be composed predominately of alkyl substituted 1,2,3,4-tetrahydronaphthalanes although there is some evidence that a very minor amount of indanes and other related compounds are produced. The alicyclic type alkylate boils very close to the alkyl benzenes having a corresponding carbon atom content. Consequently, in order to recover a satisfactory amount of the external isomers in a fraction designed to be employed as a recycle stream, it is necessary to include a substantial amount of the corresponding alicyclic alkylate present in the alkylation reaction mixture. The extent of this recovery, however, is critical since it has been ascertained that fused ring aromatic compounds formed during the alkylation reaction exhibit boiling points overlapping the upper portion of the boiling point range of the alicyclic alkylate corresponding to the external isomers sought to be recovered.

In accordance with this invention, therefore, a satisfactory recycle fraction is obtained by observing a distillation cut point within the boiling range of the alicyclic alkylate present in the bottoms fraction. In the case of an alkylate product derived from a single alkane, as much as 80% but more preferably no more than about 70% of the alicyclic alkylate present can be taken overhead without experiencing any serious contamination. Cutting this deep into the bottoms using an efficient commercial distillation tower will insure recovery of the bulk of the external alkyl benzene isomers present therein. In those instances where the alkylation reaction is carried out using a partially chlorinated alkane mixture, no apt generalization can be made as to the extent the alicyclic alkylate can be taken overhead without the inclusion of inhibiting amount of impurities. This is so because the boiling points of the inhibitors formed under such circumstances more broadly overlap the boiling point range of the alicyclic alkylate corresponding to external isomers desired to be recovered. Accordingly, in such situations the best approach is to determine experimentally for each system faced the extent of recovery applicable. To do this, one need only periodically check the overhead to determine the point at which objectional amounts of the inhibitors are being entrained. A simple arbitrary test for this purpose consists of periodically taking a portion of the overhead and heating same at a temperature of from about 40 to 80° C. in the presence of about 10% $AlCl_3$. This isomerization test is desirably conducted in a medium of benzene in order to obviate any disproportionation of the alkyl benzenes. Suitable amounts of benzene range from about 1 to 25 parts per part of the overhead. When such treatment first fails to result in more than about 75% isomerization of the external isomer content within a time period not exceeding about thirty minutes, then this will indicate that the applicable recycle cut point has been approximately reached.

Basically, the testing procedure described indicates that the accumulated fraction rich in external isomers will effectively isomerize when recycled to a conventional alkylation operation. Obviously many modifications of this test will suffice and possibly other procedures such as, for example, UV analysis, can be devised to provide the same information. Of course, in any continuous operation the proper cut point will be maintained at a given predetermined distillation temperature.

Suitable fractions rich in external isomers obtained as described above can be recycled to a reaction mixture undergoing alkylation in whole or in part. As an alternative to recycling the recovered external isomers, same can be isomerized by treatment with $AlCl_3$ and thereupon the internal isomers resulting from a direct isomerization procedure of this type can be recovered by distillation. A suitable amount of $AlCl_3$ for effecting direct isomerization is from about 2 to 10% based on the weight of the total fraction subjected to treatment. Satisfactory isomerization temperatures range from about 40 to 80° C. As indicated above, it is preferred to carry out the isomerization reaction in the presence of from about 1 to 25 parts benzene.

The much more preferred procedure from an economical standpoint for upgrading the fractions containing a rich content of external isomers, however, is to recycle them to an alkylation reactor as has been indicated throughout the previous discussion. Conventional alkylation practices are applicable in effecting the isomerization of a fraction of external isomers constituting an internal recycle stream to an alkylation reaction system. The general aspects of such practices will be discussed next.

Partially chlorinated products suitable for use in the alkylation process to which this invention is directed can be obtained by reacting between about 0.1 and 0.4 mole of chlorine per mole of paraffin. Within this range satisfactory selectivities to monochloride formation can be realized. Conventional methods for effecting the chlorination reaction can be observed, i.e., either liquid or vapor phase chlorination is applicable. The reaction can be either catalytically or thermally induced. The whole of the partially chlorinated product or dehydrohalogenated derivative thereof is customarily charged to the alkylation reaction sphere as it is too difficult to separate the converted paraffins from the unreacted paraffins.

A catalyst is required to effect the reaction between alkyl chlorides or olefins and an alkylatable compound, here specifically benzene. A variety of Friedel-Crafts catalysts are applicable. An enumeration of such catalysts include aluminum chloride, iron chloride, zinc chloride, titanium chloride, hydrofluoric acid, boron trifluoride, and the like. The preferred catalyst is aluminum chloride. In order to isomerize external isomers present in the alkylation reaction mixture as recycled material, it is necessary to use $AlCl_3$ as the alkylation catalyst. Amounts of the aluminum chloride that can be used range from between about 1 and 10% based upon the amount of alkyl chlorides present in the reaction mixture. An especially preferred catalyst system consists of aluminum chloride in admixture with catalyst sludge obtained from a previous alkylation run employing said aluminum salt as the catalyst. This affords use of substantially less aluminum chloride than is ordinarily needed to effect a given rate for the alkylation reaction. In the event the alkylating agent is an alkyl chloride, another advantage of using sludge is that aluminum powder can be incorporated in the sludge and such a mixture under the conditions of reaction encountered will provide for the in situ formation of aluminum chloride enriched sludge.

The alkylation temperature can be varied over wide limits ranging from about room temperature to 80° C. A preferred range is in the order from about 40–80° C.

The ratio of benzene to alkyl chlorides or olefins present in the reaction mixture can also be varied over wide limits. Applicable ratios are from about 1 to 20 moles benzene to 1 mole of alkyl chloride or olefin. On the aftersaid basis, a preferred range of benzene to alkyl chloride or olefin is from about 5:1 to 10:1, respectively. The alkylation reaction can be carried out in a continuous or batch manner. In either type of operation, an effective reaction time is from about 15 to 180 minutes. The precise time needed for effecting substantially complete alkylation is dependent upon a number of factors, including the amount of catalyst used, ratio of benzene to alkylating agent, temperature, etc. The course of the reaction can be readily followed by analyzing for organic chloride.

Following the alkylation reaction, it is ordinarily advantageous to treat the effluent with aqueous sulfuric acid followed by washing with caustic solution. Following this preliminary purification step, unreacted benzene is first stripped from the reaction effluent. Next, the unreacted paraffins present in the stripped mixture are removed. The reaction product is then fractionated to yield a desired composition of internal isomers and thereupon a fraction rich in external isomers is recovered in a manner described hereinabove for purposes of recycle or direct treatment with aluminum chloride to effect isomerization of the external alkyl benzene isomers present therein.

In order to illustrate further to those skilled in the art the nature of this invention and how it can be practiced, the following specific examples are given. As indicated, these examples are set forth primarily for the purposes of illustration and accordingly, any enumeration of details contained therein should not be interpreted as a limitation on the invention except as such are expressed in the appended claims. All parts are parts by weight unless otherwise indicated.

EXAMPLE I

For the purpose of illustrating the nature of the isomerization catalyst inhibitors formed in the type of alkylation procedure with which this invention is concerned, alkylation runs No. 1 and No. 2 were conducted using as the alkylating agent a partially chlorinated n-dodecane and a partially chlorinated mixture of C_{12}–C_{14} linear paraffins, respectively. Each partially chlorinated product contained about 4% combined chlorine representing about a 20% level (mole) of chlorination. In each run a benzene/alkylchloride mole ratio of 8:1, respectively, was observed and the amount of aluminum chloride alkylation catalyst was 4% based on the alkylchloride content of the alkylating agent. The alkylation reaction was carried out at 65° C.

Following alkylation, the reaction mixtures were stripped of unreacted benzene and paraffins. Thereupon, the alkylate product of each run was fractionated to yield various cuts or fractions selected to show approximately where the isomerization inhibitors occur in the product in terms of its boiling point characteristics. A portion of each cut collected was combined with an equal part of pure 2-phenyl isomer and the mixtures were then isomerized; whereupon, the extent of isomerization of the added 2-phenyl isomer was noted. In order to simplify analysis, a pure 2-phenyl tetradecane sample was employed in testing the various fractions comprising run No. 1 whereas pure 2-phenyl dodecane was used in testing the selected fractions of run No. 2. The conditions observed in carrying out the isomerization reaction were standardized using 2 parts of benzene per part of combined alkylate product and added 2-phenyl isomer and 10% $AlCl_3$ based on the latter. The isomerization reaction was conducted at 65° C. for 20 minutes. The compositions of the various cuts and results obtained are set out as follows:

TABLE I

Run No.	Cut No.	Dist. Temp.	Composition	Isomerization, percent
1	1–15	IBP–259° F. (2.5 mm. Hg)	ϕC_{12}, C_{12} alicyclic alkylate	100
1	16	259–266° F	C_{12} alicyclic alkylate	65
1	18	288–340° F	do	0
1	20	345–347° F	Diphenyl dodecane	83
1	21	347–351° F	do	89
2	1	385° F. (10 mm. Hg)	External ϕC_{13}, internal ϕC_{14}	100
2	2	385–390° F	29% int. ϕC_{14}, 51% 2-ϕC_{14}, 19% C_{14} alicyclic alkylate.	100
2	3	390–400° F	5% int. ϕC_{14}, 49% 2-ϕC_{14}, 46% C_{14} alicyclic alkylate.	100
2	4	400–420° F	98% C_{14} alicyclic alkylate*	0

*Represents about 40% of total C_{14} alicyclic alkylate present.

EXAMPLE II

The purpose of this example is to illustrate the improved results to be obtained with regard to product yield by utilizing an undesirable by-product as an internal recycle stream in accordance with this invention. The present example is limited to a process for the preparation of a tetradecylbenzene product to simplify the analyses needed for illustrating various pertinent features thereof.

To a suitable reaction vessel equipped with a stirrer and heating means were charged 7170 parts of a partially chlorinated n-tetradecane. The partially chlorinated product contained 4.53% chlorine and was prepared by chlorinating tetradecane in the liquid phase. Additionally charged to the reaction vessel were 7180 parts benzene and 107 parts aluminum chloride. These reactants were held at 65° C. for 90 minutes with stirring. Following alkylation, the reaction mixture was permitted to settle, whereupon the catalyst sludge was removed. The reaction mixture was then washed with 5% concentrated sulfuric acid, followed by washing with caustic soda solution to remove all traces of acid. The partially purified reaction mixture was then distilled to yield the following fractions:

No.	Fraction	Dist. Temp., ° C., 10 mm. Hg.	Wt. (parts)
1	Excess benzene		
2	Excess tetradecane	124–184	5,360
3		184–193	756
4		193–207	617
5	Bottoms		220

The compositions of fractions 3 and 4 were determined to be as follows:

Isomer Distribution	Fraction 3	Fraction 4
2-phenyl tetradecane	1.1	55.2
3-phenyl tetradecane	10.3	22.1
4,5,6,7-phenyl tetradecane	88.6	9.1
Alkyl substituted 1,2,3,4-tetrahydronaphthalanes		13.5

The 2-phenyl isomer content of the total alkylate (fractions 3 and 4 combined) was 30.6% when normalized on a monoalkylbenzene basis.

A second alkylation run was conducted in which the 2-phenyl isomer rich fraction 4 was employed as a recycle stream. Into an alkylation reaction vessel such as described above were charged 5352 parts of chlorinated tetradecane (4.95% chlorine), 5800 parts benzene, 86 parts aluminum chloride, and 396 parts of fraction 4. The alkylation conditions employed here corresponded essentially to those described above in connection with the previous run.

Following catalyst removal and partially purifying the reaction mixture as previously described, said mixture was then fractionated to yield the following:

No.	Fraction	Dist. Temp., ° C., 10 mm. Hg.	Wt. (parts)
6	Excess benzene		
7	Excess tetradecane	123–182	3,774
8		182–191	803
9		191–207	928
10	Bottoms		158

The composition of each of the alkylate product fractions 8 and 9 was determined to be as follows:

Isomer Distribution	Fraction 8, Percent	Fraction 9, Percent
Alkyl substituted 1,2,3,4-tetrahydronaphthalenes	1.0	19.3
2-phenyl tetradecane	2.2	41.9
3,4,5,6,7-phenyl tetradecane	96.7	38.9

The 2-phenyl tetradecane content of the total alkylate product, that is, fractions 8 and 9 combined, was 26.1% when normalized on a monoalkylbenzene basis.

EXAMPLE III

This example serves to illustrate the improved detersive properties exhibited by detergent compositions derived from monophenyl alkane mixtures which can be economically obtained in the practice of this invention.

Five alkylation runs were conducted wherein the respective alkylating stocks were various mixtures of n-dodecane, n-tridecane and n-tetradecane, all of which were chlorinated to approximately twenty mole percent. The molar ratio of alkyl chloride to benzene and the various other alkylation conditions employed were substantially identical to those conditions observed in Example II. In the initial two runs of this series, the respective alkylate products were distilled to yield fractions containing essentially all of the 2-phenyl tetradecane component of the alkylation reaction mixture. In the three subsequent runs the respective alkylation reaction mixtures were fractionally distilled, as was done in Example II, to recover monophenyl alkane fractions substantially free of 2-phenyl tetradecane. All of these alkylate products were sulfonated with 20 percent oleum and then neutralized with a caustic soda solution. The resultant sulfonate salts were compounded into a typical heavy-duty detergent composition composed of 22% of the sulfonate salt, 56% of tripolyphosphate, 17% of sodium sulfate and 5% sodium silicate. Foam stability of these several compositions was determined using the standard dishwashing test wherein 0.112 percent of the compounded detergent composition was added to water at 115° C. and thereupon uniformly soiled plates were washed until there was a permanent break in the foam covering the dishwashing pan. This test was conducted at two hardness levels. The results of this test are set forth in the following Table II.

TABLE II

Sample No.	2ϕ Alkane Content	Avg. M.W. of Alkylbenzene	Plates Washed	
			50 p.p.m. Hardness	150 p.p.m. Hardness
1	29.3	256	12.5	20.0
2	27.6	264	14.5	18.5
3	24.6	258	16.0	18.0
4	22.2	261	17.5	19.5
5	20.5	264	18.0	20.5

What is claimed is:

1. A process for the preparation of detergent alkylate which comprises alkylating an excess of benzene with a chlorination product of from about 0.1 to 0.4 mole of chlorine and a mole of a hydrocarbon selected from the group consisting of C_{10}–C_{15} linear paraffins and mixtures thereof at a temperature from about 20° C. to 80° C. in the presence of from about 1–10% $AlCl_3$ based on the alkyl chloride content of said chlorination product and in the presence of the hereinbelow-defined recycle stream, distilling the alkylation reaction mixture to recover successively a detergent alkylate fraction consisting of a mixture of secondary monophenyl alkane isomers containing a substantially reduced amount of the external secondary isomers of the highest molecular weight phenyl alkane present in the alkylation reaction mixture and a higher boiling second fraction constituting said recycle stream consisting of a mixture of said

external isomers and corresponding alicyclic alkylate but containing not in excess of that amount of the alicyclic alkylate which will result in the inclusion in said second fraction of an amount of the fused ring aromatic compounds present in the reaction mixture which would inhibit the isomerization of the external isomers under the alkylation conditions hereinabove described.

2. A process for the preparation of detergent alkylate which comprises reacting an excess of benzene at a temperature from about 20 to 80° C. with an alkylating agent obtained by dehydrohalogenating a chlorination product of from about 0.1 to 0.4 mole of chlorine and a mole of a hydrocarbon selected from the group consisting of C_{10}–C_{15} linear paraffins and mixtures thereof in the presence of from about 1–10% $AlCl_3$ based on the olefin content of the dehydrohalogenated derivative and in the presence of the hereinbelow-defined recycle stream, distilling the alkylation reaction mixture to recover successively a detergent alkylate fraction consisting of a mixture of secondary monophenyl alkane isomers containing a substantially reduced amount of the external secondary isomers of the highest molecular weight phenyl alkane present in the alkylation reaction mixture and a higher boiling second fraction constituting said recycle stream consisting of a mixture of said external isomers and corresponding alicyclic alkylate but containing not in excess of that amount of the alicyclic alkylate which will result in the inclusion in said second fraction of an amount of the fused ring aromatic compounds present in the reaction mixture which would inhibit the isomerization of the external isomers under the alkylation conditions hereinabove described.

3. A process for the preparation of detergent alkylate which comprises alkylating an excess of benzene with a chlorination product of from about 0.1 to 0.4 mole of chlorine and a mole of a linear paraffin having a carbon atom length of from 10–15 at a temperature from about 40 to 80° C. in the presence of from about 1–10% $AlCl_3$ based on the alkyl chloride content of said chlorination product and in the presence of the hereinbelow-defined recycle stream, distilling the alkylation reaction mixture to recover successively a detergent alkylate fraction consisting of a mixture of the secondary isomers of the monophenyl alkane and containing a substantially reduced amount of the external isomers thereof present in the alkylation reaction mixture and a higher boiling second fraction constituting said recycle stream consisting of a mixture of said external isomers and not in excess of about 70% of the alicyclic alkylate present in the alkylation reaction mixture.

4. A process for the preparation of detergent alkylate which comprises reacting an excess of benzene at a temperature of from about 40 to 80° C. with an alkylating agent obtained by dehydrohalogenating a chlorination product of from about 0.1 to 0.4 mole of chlorine and a mole of a linear paraffin having a carbon atom length of from 10–15 in the presence of from about 1–10% $AlCl_3$ based on the olefin content of the dehydrohalogenated derivative and in the presence of the hereinbelow-defined recycle stream, distilling the alkylation reaction mixture to recover successively a detergent alkylate fraction consisting of a mixture of the secondary isomers of the monophenyl alkane and containing a substantially reduced amount of the external isomers thereof present in the alkylation reaction mixture and a higher boiling second fraction constituting said recycle stream consisting of a mixture of said external isomers and not in excess of about 70% of the alicyclic alkylate present in the alkylation reaction mixture.

5. A process for the preparation of internal secondary isomers of a monophenyl alkane which comprises alkylating an excess of benzene with a chlorination product of from about 0.1 to 0.4 mole of chlorine and a mole of a linear paraffin having a carbon atom length of from 10–15 at a temperature from about 40 to 80°

C. in the presence of from about 1–10% $AlCl_3$ based on the alkyl chloride content of said chlorination product, distilling the alkylation reaction mixture to recover successively a first fraction consisting of a mixture of the secondary isomers of the monophenyl alkane product and containing a substantially reduced amount of the external isomers thereof present in the alkylation reaction mixture and a higher boiling second fraction consisting of said external isomers and not in excess of about 70% of the alicyclic alkylate present in the alkylation reaction mixture, heating said second fraction at a temperature between about 40 and 80° C. in the presence of from about 1 to 25 parts benzene and from 1–10% $AlCl_3$ to effect substantially complete isomerization of the external isomer content and thereupon distilling said isomerized product to recover a mixture of monophenyl alkane isomers having an isomeric distribution corresponding about to that of said first fraction.

6. A process for the preparation of detergent alkylate which comprises alkylating an excess of benzene with a chlorination product of from about 0.1 to 0.4 mole of chlorine and a mole of a C_{10}–C_{12} linear paraffin at a temperature from about 40 to 80° C. in the presence of from about 1–10% $AlCl_3$ based on the alkyl content of said chlorination product and in the presence of the hereinbelow-defined recycle stream, distilling the alkylation reaction mixture to recover successively a detergent alkylate fraction essentially free of the 2-phenyl isomer and containing a substantially reduced amount of the 3-phenyl isomer present in the alkylation reaction mixture and a higher boiling second fraction constituting said recycle stream consisting of said 2- and 3-phenyl isomers and corresponding alicyclic alkylate but containing not in excess of that amount of the alicyclic alkylate which will result in the inclusion in said second fraction of an amount of fused ring aromatic compounds present in the reaction mixture which would inhibit the isomerization of the external isomers under the alkylation conditions hereinabove described.

7. A process for the preparation of detergent alkylate which comprises alkylating an excess of benzene with a chlorination product of from about 0.1 to 0.4 mole of chlorine and a mole of a C_{10}–C_{12} linear paraffin at a temperature from about 40 to 80° C. in the presence of from about 1–10% $AlCl_3$ based on the alkyl chloride content of said chlorination product and in the presence of the hereinbelow-defined recycle stream, distilling the alkylation reaction mixture to recover successively a detergent alkylation fraction essentially free of the 2-phenyl isomer and containing a substantially reduced amount of the 3-phenyl isomer present in the alkylation reaction mixture and a higher boiling second fraction constituting said recycle stream consisting of said 2- and 3-phenyl isomers and not in excess of about 70% of the alicyclic alkylate present in the alkylation reaction mixture.

8. A process for the preparation of internal secondary isomers of a monophenyl alkane which comprises alkylating an excess of benzene with a chlorination product of from about 0.1 to 0.4 mole of chlorine and a mole of a C_{10}–C_{12} linear paraffin at a temperature from about 40 to 80° C. in the presence of from about 1–10% $AlCl_3$ based on the alkyl chloride content of said chlorination product, distilling the alkylation reaction mixture to recover successively a detergent alkylate fraction essentially free of the 2-phenyl isomer and containing a substantially reduced amount of the 3-phenyl isomer present in the alkylation reaction mixture and a higher boiling second fraction consisting of said 2- and 3-phenyl isomers and not in excess of about 70% of the alicyclic alkylate present in the alkylation reaction mixture, heating said second fraction at a temperature between about 40 and 80° C. in the presence of from about 1 to 25 parts benzene and from 1–10% $AlCl_3$ to effect substantially complete isomerization of the external isomer content and thereupon distilling said isomerized product to recover a mixture of monophenyl alkane isomers having an isomeric distribution corresponding about to that of said first fraction.

9. A process for the preparation of detergent alkylate which comprises alkylating an excess of benzene with a chlorination product of from about 0.1 to 0.4 mole of chlorine and a mole of a C_{13}–C_{15} linear paraffin at a temperature from about 40 to 80° C. in the presence of from about 1–10% $AlCl_3$ based on the alkyl content of said chlorination product and in the presence of the hereinbelow-defined recycle stream, distilling the alkylation reaction mixture to recover successively a detergent alkylate fraction essentially free of the 2- and 3-phenyl isomers and containing a substantially reduced amount of the 4-phenyl isomer and a higher boiling second fraction constituting said recycle stream consisting of a mixture of said 2-, 3-, and 4-phenyl isomers and corresponding alicyclic alkylate but containing not in excess of that amount of the alicyclic alkylate which will result in the inclusion in said second fraction of an amount of fused ring aromatic compounds present in the reaction mixture which would inhibit the isomerization of the external isomers under the alkylation conditions hereinabove described.

10. A process for the preparation of detergent alkylate which comprises alkylating an excess of benzene with a chlorination product of from about 0.1 to 0.4 mole of chlorine and a mole of a C_{13}–C_{15} linear paraffin at a temperature from about 40 to 80° C. in the presence of from about 1–10% $AlCl_3$ based on the alkyl chloride content of said chlorination product and in the presence of the hereinbelow-defined recycle stream, distilling the alkylation reaction mixture to recover successively a detergent alkylate fraction essentially free of the 2- and 3-phenyl isomers and containing a substantially reduced amount of the 4-phenyl isomer and a higher boiling second fraction constituting said recycle stream consisting of a mixture of said 2-, 3-, and 4-phenyl isomers and not in excess of about 70% of the alicyclic alkylate present in the alkylation reaction mixture.

11. A process for the preparation of internal secondary isomers of a monophenyl alkane which comprises alkylating an excess of benzene with a chlorination product of from about 0.1 to 0.4 mole of chlorine and a mole of a C_{13}–C_{15} linear paraffin at a temperature from about 40 to 80° C. in the presence of from about 1–10% $AlCl_3$ based on the alkyl chloride content of said chlorination product, distilling the alkylation reaction mixture to recover successively a detergent alkylate fraction essentially free of the 2- and 3-phenyl isomers and containing a substantially reduced amount of the 4-phenyl isomer and a higher boiling second fraction consisting of a mixture of said 2-, 3-, and 4-phenyl isomers and not in excess of about 70% of the alicyclic alkylate present in the alkylation reaction mixture, heating said second fraction at a temperature between about 40 and 80° C. in the presence of from about 1 to 25 parts benzene and from 1–10% $AlCl_3$ to effect substantially complete isomerization of the external isomer content and thereupon distilling said isomerized product to recover a mixture of monophenyl alkane isomers having an isomeric distribution corresponding about to that of said first fraction.

12. A process for the preparation of detergent alkylate which comprises alkylating an excess of benzene with the chlorination product of from about 0.1 to 0.4 mole of chlorine and a mole of a mixture of at least two but not in excess of four adjacent members of homologous series of C_{10}–C_{15} linear paraffins at a temperature of from about 40 to 80° C. in the presence of from about 1–10% $AlCl_3$ based on the alkyl chloride content of said chlorination product and in the presence of the hereinbelow-defined recycle stream, distilling the alkylation reaction mixture to recover successively a detergent alkylate fraction consisting of a mixture of secondary monophenyl alkane isomers containing a substantially reduced amount of the external secondary isomers of the highest molecular weight phenyl alkane present in the alkylation reaction mixture and a higher boiling second fraction constituting said recycle stream consisting of a mixture of said external isomers and corresponding alicyclic alkylate but containing not in excess of that amount of the alicyclic alkylate which will result in the inclusion in said second fraction of an amount of fused ring aromatic compounds present in the reaction mixture which would inhibit the isomerization of the external isomers under the alkylation conditions hereinabove described.

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