

May 9, 1972

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3,662,012

DISPROPORTIONATION OF LONG-CHAIN MONOALKYL AROMATIC COMPOUNDS

Filed July 6, 1970

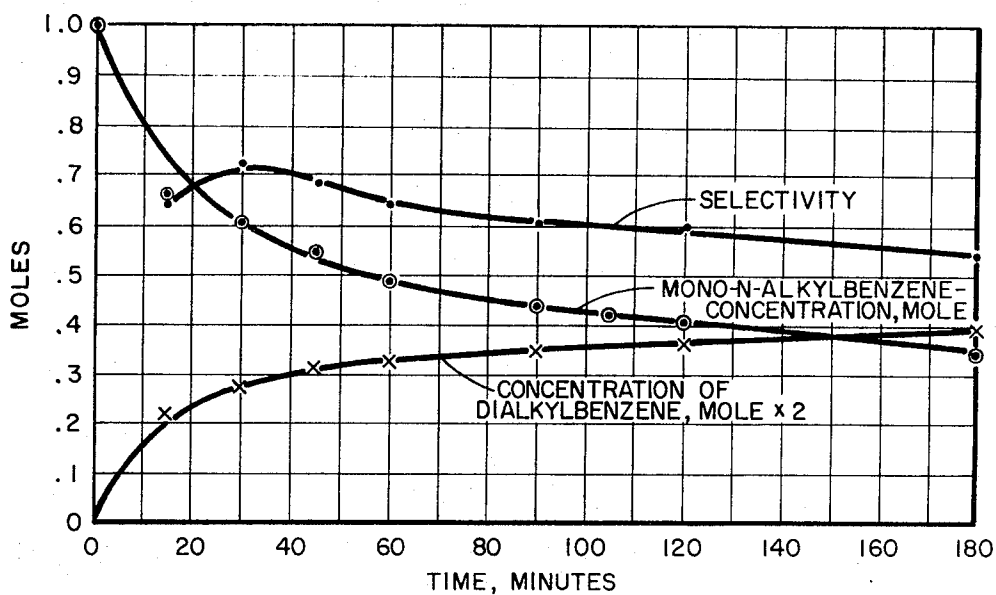


FIG. 1

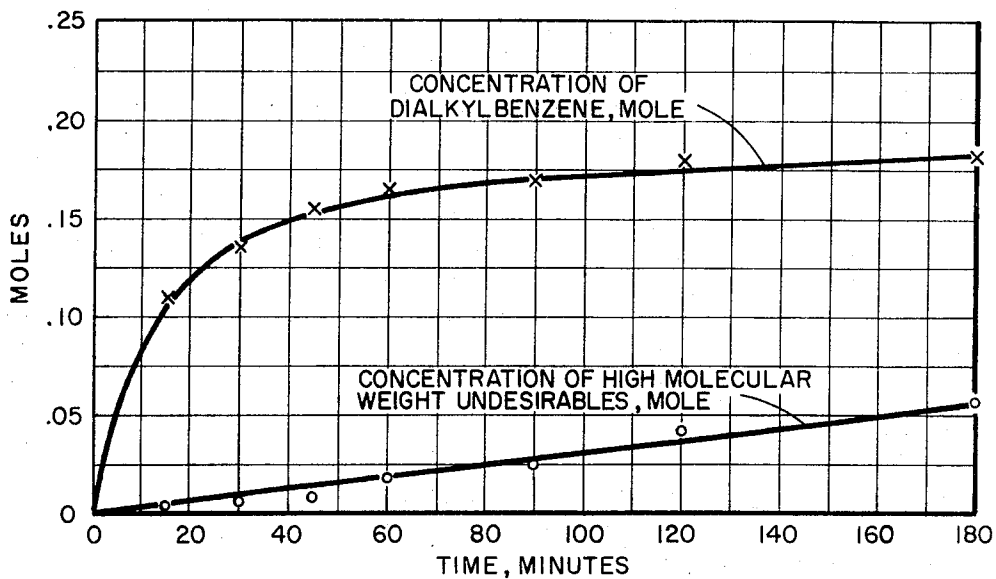


FIG. 2

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3,662,012

DISPROPORTIONATION OF LONG-CHAIN MONOALKYL AROMATIC COMPOUNDS

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Continuation-in-part of application Ser. No. 529,284, Feb. 23, 1966, which is a continuation-in-part of application Ser. No. 446,661, Apr. 8, 1965. This application July 6, 1970, Ser. No. 53,352

Int. Cl. C07c 3/62

U.S. Cl. 260—672 T

24 Claims

ABSTRACT OF THE DISCLOSURE

This disclosure concerns the preparation of a hydrocarbon composition containing a major amount of alkyl aromatic compounds having two long-chain alkyl groups and a minor amount of alkyl-substituted tetrahydronaphthalenes by the disproportionation of aromatic compounds having one long-chain alkyl group using aluminum chloride or aluminum bromide as the catalyst. The term "long-chain" refers to linear alkyl groups containing from about 8 to about 18, preferably from about 10 to about 16, carbon atoms. The hydrocarbon composition (i.e. disproportionated product) is useful as a sulfonation feedstock and as a lubricant.

RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 529,284, filed Feb. 23, 1966, which in turn was a continuation-in-part of application Ser. No. 446,661, filed Apr. 8, 1965, both now abandoned.

In addition to the above application, the following applications, which have the same assignee as the present application, are believed to be related to the subject matter of the present application.

Ser. No. 762,639, filed Sept. 25, 1968, now U.S. Pat. No. 3,538,177, concerns the disproportionation of mono-alkyl aromatic compounds to dialkyl aromatic compounds using HF—BF₃ as the catalyst. The alkyl groups of both the mono- and dialkyl aromatic compounds contain at least 8 carbon atoms. Use of the HF—BF₃ catalyst produces dialkylbenzenes without producing a significant increase in the amount of alkyl-substituted tetrahydronaphthalenes over that in the original charge stock.

DISCLOSURE

Background—Field of the invention

The present invention concerns a process for preparing hydrocarbon compositions containing a major amount of di-n-alkyl aromatic hydrocarbons, the alkyl groups each containing 8 to 18 carbon atoms. These compositions are especially useful as sulfonation feedstocks for the preparation of oil-soluble sulfonates and overbased sulfonates. It is well-known that many uses exist for oil-soluble sulfonates and overbased sulfonates. For example, oil-soluble sulfonates are useful as rust inhibitors. Millions of pounds of overbased oil-soluble sulfonates are used annually as additives in lubricating oils.

The parent applications (Ser. No. 529,284 and Ser. No. 446,661) disclosed that sulfonates prepared from di-C₈—C₁₈-n-alkaryl hydrocarbons have many improved properties as compared to sulfonates prepared from postdodecylbenzene. Postdodecylbenzene is a mixture of mono- and di-alkylbenzenes, predominantly mono-alkylbenzenes, the alkyl groups of which are branched-chain.

In addition to being useful as a sulfonation feed-stock hydrocarbon compositions containing a major amount of

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di-C₈—C₁₈-n-alkaryl hydrocarbons are also useful as low-temperature lubricants (in other words "Arctic" lubricants since they possess the requisite combination of low pour point, high viscosity index and other properties for this use). Particularly hydrocarbon compositions containing a major proportion of di-C₈—C₁₈-n-alkylbenzenes and an effective amount (e.g. about 8 to about 25 weight percent) of alkyl-substituted tetrahydronaphthalenes of similar molecular weight are very useful as low-temperature lubricants. Such compositions are prepared by the disproportionation, using aluminum chloride as the catalyst, of mono-C₈—C₁₈-n-alkylbenzenes, particularly the preferred mono C₁₀—C₁₆-n-alkylbenzenes as described herein.

Presently, it is believed that the presence of alkyl-substituted tetrahydronaphthalenes, in a composition comprising di-n-alkylbenzenes and alkyl-substituted tetrahydronaphthalenes has a beneficial effect when the composition is used as a lubricant since the alkyl-substituted tetrahydronaphthalenes lower the pour point. Moreover, when this hydrocarbon composition is used as a sulfonation feedstock the effect of the alkyl-substituted tetrahydronaphthalenes appears to be neutral, i.e. neither beneficial nor detrimental. The alkyl-substituted tetrahydronaphthalenes appear to sulfonate about as readily as the di-n-alkylbenzenes.

Since filing the parent application (Ser. No. 529,284) it has been discovered that the product prepared by disproportionation of long-chain monoalkyl aromatic compounds in addition to di-alkyl aromatic compounds contains a minor, but significant, amount of alkyl-substituted tetrahydronaphthalenes having molecular weights similar to the di-alkyl aromatic compounds. Moreover, disproportionation produces substantially more alkyl-substituted tetrahydronaphthalenes than does alkylation, i.e. the preparation of di-alkyl aromatic compounds by alkylation of mono-alkyl aromatic compounds.

Also, in the parent application the catalyst was broadly described as being a Friedel-Crafts catalyst, with aluminum chloride and aluminum bromide being preferred. Subsequent work has shown that not all Friedel-Crafts catalysts, particularly the weaker catalysts such as ferric chloride, BF₃ alone, BF₃ plus water, aluminum chloride-nitrobenzene and aluminum chloride-nitromethane, result in the disproportionation of mono-n-alkylbenzenes to di-n-alkylbenzenes.

The use of HF—BF₃ as a catalyst does result in disproportionation of mono-n-alkylbenzenes to di-n-alkylbenzenes. However, the use of HF—BF₃ as a catalyst requires different operating conditions, particularly temperature, than does aluminum chloride. More importantly, disproportionation of monoalkylbenzenes using HF—BF₃ does not result in a significant amount of alkyl-substituted tetrahydronaphthalenes in the disproportionated product. By contrast, the use of aluminum chloride or aluminum bromide does result in a significant amount of alkyl-substituted tetrahydronaphthalenes in the disproportionated product.

PRIOR ART

According to the references cited in the parent application, Ser. No. 529,284, the following patents are the most pertinent references:

U.S. 2,753,384—Lien et al.—This reference teaches a process for the disproportionation of mono-n-alkylbenzenes to the corresponding di-n-alkylbenzenes using HF—BF₃ as the catalyst. According to Lien et al. butyl is the longest alkyl group suitable in their process with propyl being preferred. In column 4, lines 39—43, Lien et al. state "The n-butylbenzenes undergo cracking and other side reactions more readily than the n-propylbenzenes." In addition Lien et al. state "The invention is limited to the

HF—BF₃ treatment of propylbenzene and butylbenzene because successful treatment of the pentybenzene requires different operating conditions" (col. 5, lines 47-40).

U.S. 2,993,939—Raley et al.—This reference, which is concerned with isomerization of alkylaromatics, teaches that in the prior art isomerization work AlCl₃ and HF—BF₃ were considered equivalent as isomerization catalysts.

With regard to this reference applicants believe that it is well-recognized that isomerization and disproportionation are entirely different processes.

BRIEF SUMMARY OF THE INVENTION

Broadly stated, the present invention concerns a process for preparing alkyl aromatic compounds having two long-chain alkyl groups by the disproportionation of mono long-chain alkyl aromatic compounds using aluminum chloride or aluminum bromide as the catalyst.

In one aspect, our invention concerns a process for preparing a hydrocarbon composition containing a major amount of alkyl aromatic compounds having two long-chain alkyl groups and a minor, but significant, amount of alkyl-substituted tetrahydronaphthalenes of similar molecular weight by the disproportionation of alkyl aromatic compounds containing one long-chain alkyl group using aluminum chloride or aluminum bromide as the catalyst.

In another aspect, our invention concerns a process for preparing a hydrocarbon composition containing from about 64 to about 85 weight percent long-chain dialkylbenzenes and from about 8 to about 25 weight percent alkyl-substituted tetrahydronaphthalenes of similar molecular weight by the disproportionation, using aluminum chloride or aluminum bromide as the catalyst, of the product resulting from the alkylation of benzene with a halogenated, preferably chlorinated, paraffin as described herein.

In still another aspect, our invention concerns the products prepared by any of the processes described in the foregoing.

The term "long-chain" as used in the foregoing refers to linear alkyl groups containing from about 8 to about 18, preferably from about 10 to about 16, carbon atoms.

Preferably, the alkyl aromatic compound containing one long-chain alkyl group and the alkyl aromatic compound containing two long-chain alkyl groups are mono-n-C₈-C₁₈ alkylbenzene and di-n-C₈-C₁₈ alkylbenzene, respectively.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing the rate of conversion of mono-n-alkylbenzene, and the rate of production of di-n-alkylbenzenes as the disproportionation reaction proceeds.

FIG. 2 is a graph showing the manner in which the yields of di-n-alkylbenzenes and undesirable higher molecular weight products increase with increasing disproportionation reaction time and consequent increase in the extent of conversion of mono-n-alkylbenzene.

The di-n-alkylbenzene fraction described in FIG. 2 also contains a minor amount of alkyl-substituted tetrahydronaphthalenes of similar molecular weight.

DETAILED DESCRIPTION

The mono-n-alkaryl compounds

In the disproportionation process of our invention a suitable starting material consists essentially of mono-n-alkaryl compounds of a certain specific character. More specifically described, these mono-n-alkaryl compounds are characterized in having an aromatic nucleus which is mono-substituted by a straight-chain or normal alkyl group containing from 8 to 18 carbon atoms and attached to the aryl group through a secondary carbon atoms. The aromatic moiety of the mono-n-alkaryl compounds can be

phenyl, tolyl, or xylyl, but preferably is phenyl. It is preferable that the alkyl substituents of the compounds contain from 10 to 16 carbon atoms and most preferred that the alkyl substituent not differ by more than 4 carbon atoms in chain length.

The term mono-n-alkaryl compounds as used herein refers to alkaryl compounds containing one long-chain (C₈-C₁₈) alkyl group, it being understood that when the aryl moiety is tolyl one methyl group is on the aromatic nucleus and when the aryl moiety is xylyl two methyl groups are on the aromatic nucleus.

Any mono-n-alkaryl hydrocarbon meeting the description stated immediately above can be used in our process. Examples of suitable "pure" mono-n-alkaryl hydrocarbons include decylbenzene, undecylbenzene, dodecylbenzene, tridecylbenzene and tetradecylbenzene. In addition mixtures of mono-n-alkaryl hydrocarbons, such as those described, can be used.

A particularly suitable source of starting material is the detergent alkylate described in U.S. Pat. No. 3,316,294. This alkylate is rich in mono-n-alkaryl compounds meeting the definition above, and can be used in the method of the present invention without further purification or treatment. Usually the detergent alkylate will contain at least 90 weight percent mono-n-alkaryl compounds of the type described. Also the mono-n-alkaryl compounds in the detergent alkylate are characterized in having at least 95 percent of the alkyl groups bonded to the aryl nucleus through a secondary carbon atom of the respective alkyl group.

Briefly, the process of U.S. 3,316,294 comprises the following steps, broadly stated: (a) separating a fraction of substantially straight-chain C₈-C₁₈ hydrocarbons or fraction thereof from a petroleum distillate substantially free of olefins and containing said straight-chain hydrocarbons together with non-straight chain hydrocarbons, (b) chlorinating said fraction to the extent whereby between about 10 and about 35 mole percent of the straight-chain hydrocarbons present are substantially only monochlorinated, and (c) alkylating an aromatic compound, e.g. benzene, with the chlorination product of step (b) in the presence of an alkylation catalyst.

Mono-n-alkylbenzenes of the type prepared by U.S. 3,316,294 are available under the trademarks "Nalkylene" 500 and "Nalkylene" 600 from Continental Oil Company. These particular materials have the following typical properties:

"NALKYLENE" 500

Test	Typical value	Test method
Boiling range (° F.)	535-595	ASTM D-447.
Bromine number	1 0.05	ASTM D-1158.
Average molecular weight	231-241	Mass spec.
Color, Saybolt	-25	
Specific gravity (20/20)	0.85-0.87	ASTM D-287.
Viscosity (Saybolt seconds)	2 40-45	ASTM 88-44.

"NALKYLENE" 600

Boiling range (° F.):		
8%.....	530-590	ASTM D-477.
95%.....	600-615	ASTM D-477.
Bromine number	1 0.05	P.M. #21.
Average molecular weight	255-264	Mass spec.
Color, Saybolt	2 25	P.M. #20.
Specific gravity	0.85-0.87	ASTM D-287.
Viscosity (Saybolt seconds)	2 40-46	ASTM 88-44.

¹ Maximum.

² At 100° F.

³ Minimum.

While we believe that we have provided an adequate description of the salient features of U.S. 3,316,294, in order to make our disclosure even more complete this patent is made a part of this disclosure.

THE CATALYST

The catalyst in the process of our invention is restricted to aluminum chloride, aluminum bromide or mixtures thereof. The discussion provided under the heading "Back-

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ground—Field of the invention” has shown why the catalyst is restricted to these materials. Since aluminum chloride is less expensive it is the preferred catalyst.

A suitable amount of catalyst is from about 0.1 to about 10 weight percent, based on the monoalkaryl starting material. Preferably, the amount of catalyst is from about 0.5 to about 3 weight percent on the same basis. When a temperature of 100° C. is employed in the process the most preferred amount of catalyst is about 0.5 weight percent.

When using aluminum chloride or aluminum bromide as a catalyst it is advantageous to include therewith a small amount of a proton-donor material (often called a promoter), such as water or HCl. (This feature is believed to be well-known and, therefore, does not constitute a part of our invention.) In our process the amount of proton-donor material is typically about 4 weight percent based on the weight of catalyst.

PROCESS CONDITIONS

While the disproportionation process can be conducted using a temperature in the range of from about 20° C. to about 130° C., we have found that more suitably the temperature employed is in the range of from about 75° C. to about 120° C. This is because maximum yields of the desired disproportionated product are obtained in reasonable reaction times (e.g. 5 to 120 minutes) using these latter-mentioned temperatures. The most preferred temperature for use in the disproportionation process is about 100° C. The term “disproportionated product” refers to the hydrocarbon composition consisting essentially of di-n-alkyl aromatic hydrocarbons and alkyl-substituted tetrahydronaphthalenes described elsewhere herein. Also, the term disproportionated product is equivalent to the term di-n-alkaryl product as described on pages 54 and 55 of Ser. No. 529,284.

The reaction time for the disproportionation process is at least five minutes and preferably is in the range of from about thirty minutes to about three hours, depending upon catalyst level and reaction temperature.

On the basis of present knowledge it is believed that higher operating temperatures result in an increase in the amount of alkyl-substituted tetrahydronaphthalenes in the disproportionated product.

The disproportionation reaction can be carried out by either a continuous or a batch process.

When the described preferred conditions and preferred amounts of material are utilized, from about 30 to 60 mole percent of the mono-n-alkaryl starting material is converted to products. The products include di-n-alkaryl compounds, alkyl-substituted tetrahydronaphthalenes, relatively low molecular weight aromatic compounds, and relatively low molecular weight branched-chain alkane compounds. There are also small amounts of undesirable higher molecular weight materials, such as naphthalenes, trialkaryl compounds and polyphenylalkanes. These higher molecular weight materials are difficult to separate from the disproportionated product,¹ and lower the yield and quality of the oil soluble sulfonate compositions produced from the disproportionated product in the manner hereinafter described. We have found that the quantity of these undesirable high molecular weight products can be minimized by controlling the reaction conditions and, particularly, the temperature, amount of catalyst and reaction time, so as to limit the amount of mono-n-alkaryl starting material which is converted to product to from about 30 to about 50 mole percent. At this extent of conversion, selectivity to the desired disproportionated product is maximum and is from about 75 percent to 95 percent. This will be better understood when reference is made to examples hereinafter appearing, and to the accompanying drawings.

¹As stated previously herein, the term “disproportionated product” refers to a hydrocarbon composition consisting essentially of di-n-alkylaromatic hydrocarbons and alkyl-substituted tetrahydronaphthalenes of similar molecular weight.

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After cessation of the reaction process the lower boiling benzene and paraffin co-products, and the unreacted monoalkylbenzene, are removed by distillation. The distillation cut point used to insure removal of these lower boiling components varies, being dependent on the molecular weight of the monoalkylbenzenes. Knowing the molecular weights of the monoalkylbenzenes and the desired disproportionated product anyone skilled in the art, without undue experimentation, can determine a satisfactory cut point.

Since in the present invention the alkyl groups contain from 8 to 18 carbon atoms the distillation cut point for removing unreacted monoalkylbenzene would vary from that of octylbenzene to octadecylbenzene. These limits are as follows:

	Distillation cut point at—	
	10 mm., ° C.	760 mm., ° C.
Octylbenzene.....	125	270
Octadecylbenzene.....	240	425

The above cut points represent the extremes. As one example of a typical usual situation, when starting material is a mixture of C₁₂–C₁₄ monoalkylbenzenes (e.g. “Nalkylene” 600 described hereinbefore) the cut point would be about 205° C. at 10 mm. or 276° C. at 760 mm. pressure.

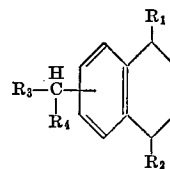
The unreacted mono-n-alkaryl compounds can be recovered from the overhead and recycled to the process.

THE DISPROPORTIONATED PRODUCT

The disproportionated product consists essentially of dialkaryl compounds, preferably di-n-C₈–C₁₈-alkylbenzenes, and alkyl-substituted tetrahydronaphthalenes of similar molecular weight. In addition it can contain minor amounts of alkyl-substituted indanes, indenenes, diphenylalkanes, naphthalenes and alkyl-substituted naphthalenes.

As used herein the term dialkaryl compounds refer to alkaryl compounds containing two long-chain (C₈–C₁₈) alkyl groups. It is understood that when the aryl moiety is tolyl or xylyl there is present one or two methyl groups, in addition, respectively.

When the starting material is a monoalkylbenzene the alkyl-substituted tetrahydronaphthalenes in the disproportionated product have the following structural formula:



wherein R₁ and R₂ contain from 1 to 13 carbon atoms each, with the sum of R₁ and R₂ being from about 4 to about 14, and R₃ and R₄ contain from 1 to about 16 carbon atoms each, with the sum of R₃ and R₄ being from about 7 to about 17. The alkyl groups R₁, R₂, R₃, and R₄ are predominantly straight chain.

When the starting material is a monoalkylaromatic compound, wherein the aryl moiety is tolyl or xylyl, the alkyl-substituted tetrahydronaphthalenes in the disproportionated product have a formula similar to that shown above except the aryl moiety contains one or two methyl groups, respectively.

Typically, the disproportionated products, produced by the process of our invention, have the following chemical composition, as indicated by mass spectrometer analysis:

Component:	Percent by weight
Dialkaryl compounds ¹	64-85
Alkyl-substituted tetrahydronaphthalenes ² ..	8-25
Indenes, less than	4
Diphenylalkanes, less than	5
Naphthalenes and alkyl-substituted naphthalenes, less than ³	2

¹ Preferably dialkylbenzenes.

² Contains trace amounts of alkyl-substituted indanes.

³ Referred to as undesirable high molecular weight compounds hereinbefore.

Physical properties of typical disproportionated products, prepared by the process of our invention, are shown below.

Using a material such as "Nalkylene" 500 and operating within the process conditions described in the foregoing, the disproportionated product (cut point of 165° C. at 5 mm. Hg) has the following physical properties:

	Suitable	Preferred
Viscosity, ° F., c.s.:		
-40	5,000-10,000	6,000-9,000
100	20.3-30.0	22.7-25.0
210	4.0-4.8	4.1-4.5
Viscosity index	80-100	84-93
Pour point, ° F.	-55-90	-65-80
Molecular weight	350-400	375-385

Similarly, using a material such as "Nalkylene" 600 and operating within the process conditions described in the foregoing the disproportionated product (cut point of 197° C. at 5 m. Hg) has the following physical properties:

	Suitable	Preferred
Viscosity, ° F., c.s.:		
-40	7,600-17,600	9,000-13,000
100	24.5-37.0	28.0-33.0
210	4.4-6.1	5.0-5.8
Viscosity index	105-126	108-115
Pour point, ° F.	-40-80	-60-75
Molecular weight	375-475	400-460

In order to disclose more clearly the nature of the present invention the following examples, both illustrative and comparative, are provided. It should be clearly understood, however, that this is done solely by way of example and is not to be construed as a limitation upon the spirit and the scope of the appended claims.

Examples 1-6 below correspond to Examples 18-23 of Ser. No. 529,284, with the exception that the examples now state that a minor amount of alkyl-substituted tetrahydronaphthalenes are present in the dialkylbenzene fraction.

Example 1.—200 grams of n-decylbenzene were placed in a 500 ml. flask and heated to a temperature of 75° C. 4 grams of aluminum chloride were then placed in the flask with a trace of water and stirring was commenced. After 45 minutes, 53 percent of the n-decylbenzene had reacted to give a total reaction mixture which, by gas liquid partition chromatography, contained:

Component:	Weight percent
n-Decylbenzene	47.0
AlCl ₃ sludge	3.0
C ₁₀ paraffins	4.0
Benzene	9.0
Diphenyl decane	0.5
Heavy bottoms	1.0
Dialkylbenzene ¹	35.5

¹ A minor amount of alkyl-substituted tetrahydronaphthalenes was present in this fraction.

Example 2.—A disproportionation reaction was carried out using the conditions set forth in Example 1 and employing n-decylbenzene as the n-alkaryl starting material. Samples were removed from the reaction mixture at 15 minute intervals following the commencement of the re-

action and were analyzed by gas liquid partition chromatography. From this analysis, the extent of depletion or conversion of the n-decylbenzene starting material was determined, and the percent selectivity to the desired di-n-decylbenzene product was calculated. The group depicted in FIG. 1 of the drawings illustrates the manner in which the concentration of the di-n-decylbenzene product ² and mono-n-decylbenzene starting material varied as the reaction progressed. The graph also shows the variation with time of the selectivity to the desired di-n-decylbenzene.²

It will be noted in referring to FIG. 1 that maximum selectivity to the desired product occurred between about 18 and 58 minutes following the time of commencement of the reaction. Stated differently, maximum selectivity to the desired di-n-alkaryl product appears to occur at a time when from about 30 mole percent to about 50 mole percent of the starting material has been converted to product.

It was determined that when the disproportionation reaction is conducted to a stage where less than 30 percent conversion of the starting material has occurred, the amount of catalyst complex sludge which is produced by the reaction in relation to the total amount of starting material converted to the desired product results in lower selectivity. On the other hand, if the reaction is permitted to proceed to the point where over 50 percent conversion of the starting material takes place, the selectivity is also lowered and a considerably larger concentration of undesirable high molecular weight compounds results. The relationship of the time over which the reaction has proceeded to the concentration in the product of the undesirable high molecular weight material is depicted in FIG. 2 of the drawings.

Example 3.—This example illustrates the preparation of a di-n-alkylbenzene alkylate from a detergent alkylate prepared by the process of U.S. 3,316,294, and corresponding to "Nalkylene" 600 described hereinbefore, using the disproportionation procedure. This detergent alkylate was determined by mass spectrometer analysis to have the following composition:

Component:	Weight percent
Mono-n-alkylbenzene	92.8
Diphenylalkane
Tetrahydronaphthalenes	7.1
Naphthalenes	0.1
Average molecular weight	261

The detergent alkylate was further analyzed by mass spectrometer and gas liquid partition chromatography for molecular weight distribution and isomeric content as follows:

Alkyl chain length:	Weight percent	
	Mass spec.	GLPC
C ₁₀	0.1
C ₁₁	1.60	1.6
C ₁₂	17.2	15.2
C ₁₃	54.6	51.4
C ₁₄	26.4	26.9
C ₁₅	0.2	4.6

Number ¹	Weight percent
1 (Primary)	0.5
2 (Secondary)	24.4
3 (Secondary)	15.9
4 (Secondary)	16.3
5 (Secondary)	17.9
6 (Secondary)	17.1
7 (Secondary)	8.0

¹ Alkyl group carbon atom attached to benzene.

² A minor amount of alkyl-substituted tetrahydronaphthalenes was present in this fraction.

The detergent alkylate as thus produced was continuously pumped into a two stage disproportionation reactor unit. One weight percent of AlCl_3 catalyst based on the weight of the detergent alkylate was continuously added to the first reactor stage with a trace of HCl . The reacting material was then permitted to move into the second reactor stage after addition of the catalyst. The residence time in the two stage reactor was 3 hours. Both stages of the reactor were held at 75°C .

A sample of the product developed in the second reactor was collected and the sludge removed therefrom. Analysis of the sludge-free sample indicated that disproportionation of the detergent alkylate under these conditions resulted in a conversion of 33.5 mole percent of the detergent alkylate starting material. On the basis of the total detergent alkylate consumed in the reaction, the weight percent yields of the various products with the exception of a very small amount of high molecular weight product were as follows:

Di-n-alkylbenzene ¹	67.3
n-Paraffins	12.7
Sludge	5.7
Benzene	13.7

¹ A minor amount of alkyl-substituted tetrahydronaphthalenes was present in this fraction.

Example 4.—The di-n-alkylbenzene product of the disproportionation reaction described in Example 3 was isolated by fractionation and was then subjected to sulfonation by initially placing 1,500 grams of the di-n-alkylbenzene and 1,210 grams of 100 pale oil in a reaction flask. This mixture was contacted with 2,250 grams of 20 percent oleum under sulfonation conditions. A yield of 1.2 pound of oil soluble sulfonic acid per pound of the di-n-alkylbenzene disproportionation reaction product was obtained from the sulfonation reaction.

Example 5.—3,000 grams of the detergent alkylate described in Example 3 was contacted at 100°C . and for a period of two hours with 15 grams of aluminum chloride activated by a trace of HCl . 47 mole percent of the detergent alkylate was converted to products and the yield of di-n-alkylbenzene was 0.7 pound per pound of the detergent alkylate consumed.

Example 6.—1,000 grams of the detergent alkylate described in Example 3 was contacted at 100°C . for a period of 2.5 hours with 5 grams of aluminum chloride activated by a trace of HCl . 47.3 mole percent of the detergent alkylate was converted to products and 0.71 pound of di-n-alkylbenzene was produced for each pound of the alkylate consumed.

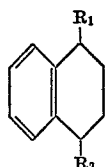
Example 7.—This example illustrates the invention and shows that the use of AlCl_3 as the catalyst results in a substantial increase in the amount of tetrahydronaphthalenes.

The monoalkylate composition used as the starting material was produced by the process of U.S. 3,316,294 and had the following analysis:

	Mole or weight percent
Monoalkylbenzenes ¹	89.5
Tetrahydronaphthalenes ²	10.5

¹ C_{11} — C_{14} alkyl groups, with a predominance of C_{13} .

² Represented by the formula:



wherein R_1 and R_2 contain from 1 to 13 carbon atoms each, with the sum of R_1 and R_2 being from about 4 to about 14.

An amount of 1,500 grams of the monoalkylate composition was charged to an autoclave. To this were added 20 grams AlCl_3 (1.3% by weight based on monoalkylate) and 0.3 gram water. The contents of the autoclave were stirred for 2 hours while maintaining the temperature at 110°C . The reaction mixture was then settled and the catalyst withdrawn. The reaction product was washed with an aqueous base. Following this the reaction product was fractionally distilled using a cut-point of 197°C . at 10 mm. Hg. The product (bottoms fraction) had a yellow to brown color. It contained 67.1% dialkylbenzenes³ and 24.4% alkyl-substituted tetrahydronaphthalenes, with the remaining 8.5% being a mixture of naphthalenes, dihydronaphthalenes, and diphenylalkanes. The product had the following physical properties:

Pour point, $^\circ\text{F}$	-65
Viscosity at -40°F	12,066
Viscosity at 100°F	32.84
Viscosity at 210°F	5.41
Viscosity index	110

Example 8.—This example is comparative and shows that the use of HF-BF_3 as the catalyst does not result in any substantial increase in the amount of tetrahydronaphthalenes, in the disproportionated product as compared to the starting material.

The monoalkylate composition used as a starting material (charge stock) was the same as in Example 7.

An amount of 900 grams of the monoalkylate composition was charged to an autoclave. The BF_3 (50 grams) and HF (500 grams) were then added to the autoclave. This reaction mixture was stirred for 1 hour with the temperature at 25°C . The reaction mixture was then settled and the catalyst withdrawn. The reaction product was washed with an aqueous base. Following this the reaction product was fractionally distilled using a cut-point of 197°C . at 10 mm. Hg. The desired product (bottoms fraction) was water-white. It contained 87.7% dialkylbenzenes⁴ and 12.1% alkyl-substituted tetrahydronaphthalenes. It had the following physical properties:

Pour point, $^\circ\text{F}$	-60
Viscosity at -40°F , cs.	6795
Viscosity at 100°F , cs.	27.05
Viscosity at 210°F , cs.	4.93
Viscosity index	119

Example 9.—This example is comparative and shows the effect of using catalysts other than aluminum chloride or HF-BF_3 complex. In all runs the monoalkylate composition was the same as in Example 7. The various catalysts tested and the results obtained are shown below.

Catalyst:	Result
Ferric chloride	No disproportionation reaction.
BF_3 (alone)	Do.
AlCl_3 -nitrobenzene	Do.
HF (alone)	Product had very high viscosity at -40°F .
BF_3 +water	No disproportionation reaction.
AlCl_3 -nitromethane	Do.

³ The percent conversion of monoalkylbenzenes to dialkylbenzenes was 45%.

⁴ The percent conversion of monoalkylbenzenes to dialkylbenzenes was 56%

Example 10.—This example illustrates the preparation of a large batch of the disproportionated product by a continuous reaction process.

The starting material (charge stock) was "Nalkylene" 600 detergent alkylate described hereinbefore.

The reaction vessel was a 3000-gallon, stirred-kettle reactor, fitted for heating, controlled addition of liquids and solids and introduction of gaseous materials. "Nalkylene" 600 detergent alkylate and AlCl_3 were fed continuously to the reaction vessel at rates of $150 \pm \text{s.c.f.}$ per minute. The level of reaction mass in the reactor was maintained to afford a residence time of 1.75 ± 0.25 hours. The reaction temperature was in the range of 90 to 95° C. As the crude product was removed continuously from the reactor monitoring by GLPC analysis indicated that it contained 5 wt. percent benzene, 15 wt. percent paraffins, 55 wt. percent unreacted monoalkylbenzene and 25 wt. percent dialkylbenzenes. The crude product was allowed to settle and the AlCl_3 sludge was removed. The remaining crude product was then contacted with 2 volumes of 15±10 wt. percent caustic solution. Following this, the crude product was contacted with 4±1 volumes of water to remove the residual caustic. The neutralized crude product was then distilled recovering the following fractions:

benzene—70–225° F. at 750 mm. Hg.
paraffins—225–290° F. at 10 mm. Hg.
monoalkylbenzene—290–330° F. at 12 mm. Hg.
disproportionation product—above 330° F. at 12 mm. Hg.

The disproportionation product was subjected to a further fractionation to remove 85±10 wt. percent overhead boiling between 450° and 850° F. at 760 mm. Hg. The residue was set aside. The overhead product was the desired disproportionated product. (164,000 pounds were produced.) The disproportionated product had the following physical properties:

Viscosity, cs.:
—40° F. ----- 9196
100° F. ----- 29.06
210° F. ----- 5.02
Pour point, ° F. ----- -75
Flash point, COC, ° F. ----- 448
Fire point, COC, ° F. ----- 500

It had the following chemical analysis: ⁵

Component:	Weight percent
Dialkylbenzenes -----	74.3
Alkyl-substituted tetrahydro-naphthalenes ----	19.1
Diphenylalkanes -----	2.0
Indenes -----	2.5
Miscellaneous -----	2.1

⁵ By mass spectrometry.

Example 11.—A series of comparative runs were made preparing dialkylbenzene from monoalkylbenzene by disproportionation and by realkylation. The monoalkylbenzene used in these runs was prepared from high purity individual molecular weight n-paraffin (e.g. a substantially pure dodecane). The paraffin was first chlorinated, then the chlorinated paraffin was used to prepared the monoalkylbenzene (by alkylation).

The dialkylbenzenes were prepared by (1) disproportionation of the monoalkylbenzene or (2) alkylation of the monoalkylbenzene with the chlorinated paraffin.

In seven of the ten sets of runs made the product prepared by disproportionation contained alkyl-substituted tetrahydronaphthalenes.

Using dodecylbenzene, prepared from n-dodecane as the starting material, the products had the following compositions (volume percent):

	Process	
	Alkyl-ation	Disproportionation
5 Dialkylbenzene.....	96	79
10 Alkyl-substituted tetrahydronaphthalenes.....	2	16
Miscellaneous.....	2	5

Example 12.—This example illustrates the use of aluminum bromide as the catalyst in the disproportionation process of our invention.

The starting material (charge stock) was a "Nalkylene" 600 containing 9.5% tetrahydronaphthalenes, with the remainder being substantially all mono-n-alkyl-benzenes.

The amounts of materials were as follows:

	G.
"Nalkylene" 600 -----	265
AlBr_3 -----	4.8
HCl (trace)	

¹ 2% by weight of mono-n-alkylbenzenes in charge stock—this is equal to 1% AlCl_3 on a mole basis.

The reaction was conducted at 75° C. for 3 hours. Using a cut-point of 205° C. at 10 mm. the amount of bottom product was 76.7 grams, a yield of 63% based on alkylate consumed. The reaction had a 45.6% conversion.

The bottoms product had the following analysis by mass spectrometry.

	Vol. percent
Di-n-alkylbenzene -----	70.9
Alkyl-substituted tetrahydronaphthalenes -----	23.6
Miscellaneous -----	5.6

Having thus described the invention by providing specific examples thereof, it is to be understood that no undue limitations or restrictions are to be drawn by reason thereof and that many variations and modifications are within the scope of the invention.

The invention having thus been described, what is claimed and desired to be secured by Letters Patent is:

1. A process for preparing alkyl aromatic compounds having two linear alkyl groups, each of which contains from about 8 to about 18 carbon atoms, the aryl moiety of said compounds being selected from the group consisting of phenyl, tolyl, xylyl, and mixtures thereof, said process consisting essentially of:

(a) contacting alkyl aromatic compounds having one linear alkyl group containing from about 8 to about 18 carbon atoms and the aryl moiety being selected from the group consisting of phenyl, tolyl, xylyl, and mixtures thereof, with from about 0.1 to about 10 weight percent of a catalyst selected from the group consisting of aluminum chloride, aluminum bromide and mixtures thereof, based on said alkyl aromatic compounds having one linear alkyl group, at a temperature of from about 20° C. to about 130° C. and for a time of from about 5 to about 180 minutes,

(b) separating by fractional distillation from the reaction product of step (a) said alkyl aromatic compounds having two linear alkyl groups, each of which contains from about 8 to about 18 carbon atoms.

2. The process of claim 1 wherein the reaction temperature of step (a) is from about 75 to about 120° C.

3. The process of claim 2 wherein the catalyst is aluminum chloride and the amount of catalyst is from about 0.5 to about 3 weight percent.

4. The process of claim 3 wherein the reaction time of step (a) is from about 30 to about 180 minutes.

5. The process of claim 4 wherein the linear alkyl group of the alkyl aromatic compounds of step (a) and both linear alkyl groups of the alkyl aromatic compounds of the product in step (b) contain from about 10 to about 16 carbon atoms.

6. The process of claim 5 wherein the reaction temperature is about 100° C.

7. A process preparing dialkylbenzenes having two linear alkyl groups each of which contains from about 8 to about 18 carbon atoms wherein said process consists essentially of:

(a) contacting monoalkylbenzenes, the alkyl groups of which contain from about 8 to about 18 carbon atoms and are linear with from about 0.1 to about 10 weight percent of a catalyst selected from the group consisting of aluminum chloride, aluminum bromide and mixtures thereof, based on said monoalkylbenzenes, at a temperature of from about 20° C. to about 130° C. and for a time of from about 5 to 180 minutes,

(b) separating by fractional distillation from the reaction product of step (a) said dialkylbenzenes.

8. The process of claim 7 wherein the reaction temperature of step (a) is from about 75 to about 120° C.

9. The process of claim 8 wherein the catalyst is aluminum chloride and the amount of catalyst is from about 0.5 to about 3 weight percent.

10. The process of claim 9 wherein the alkyl group of the monoalkylbenzenes and both alkyl groups of the dialkylbenzenes contain from about 10 to about 16 carbon atoms.

11. The process of claim 10 wherein the alkyl groups of the monoalkylbenzenes and both alkyl groups of the dialkylbenzenes are attached to the benzene ring through a secondary carbon atom.

12. The process of claim 11 wherein the reaction temperature is about 100° C.

13. A process for preparing a hydrocarbon composition containing a major amount of alkyl aromatic compounds, said compounds having two linear alkyl groups containing from about 8 to about 18 carbon atoms and the aryl moiety being selected from the group consisting of phenyl, tolyl, xylyl and mixtures thereof, and a minor amount of alkyl substituted tetrahydronaphthalenes, said process consisting essentially of:

(a) contacting alkyl aromatic compounds having one linear alkyl group containing from about 8 to about 18 carbon atoms and the aryl moiety being selected from the group consisting of phenyl, tolyl, xylyl, and mixtures thereof, with from about 0.1 to about 10 weight percent of a catalyst selected from the group consisting of aluminum chloride, aluminum bromide and mixtures thereof, based on said alkyl aromatic compounds having one linear alkyl group, at a temperature of about 20° C. to about 130° C. and for a time of from about 5 to about 180 minutes,

(b) separating by fractional distillation from the reaction product of step (a) said hydrocarbon composition containing a major amount of alkyl aromatic compounds having two linear alkyl groups and a minor amount of alkyl substituted tetrahydronaphthalenes.

14. The process of claim 13 wherein the product is a hydrocarbon composition containing from about 64 to about 85 weight percent alkyl aromatic compounds having two linear alkyl groups and from about 8 to about 25 weight percent alkyl-substituted tetrahydronaphthalenes.

15. The process of claim 14 wherein the reaction temperature of step (a) is from about 75 to about 120° C.

16. The process of claim 15 wherein the catalyst is aluminum chloride and the amount of catalyst is from about 0.5 to about 3 weight percent.

17. The process of claim 16 wherein the reaction temperature is about 100° C.

18. A process for preparing a hydrocarbon composition containing from about 64 to about 85 weight percent dialkylbenzenes the alkyl group of which contain from about 8 to about 18 carbon atoms, and from about 8 to about 25 weight percent alkyl-substituted tetrahydronaphthalenes, said process consisting essentially of:

(a) contacting monoalkylbenzenes, the alkyl groups of which contain from about 8 to about 18 carbon atoms and are linear, with from about 0.1 to about 10 weight percent aluminum chloride or aluminum bromide catalyst, based on said monoalkylbenzenes, at a temperature of from about 20° C. to about 130° C. and for a time of from about 5 to about 180 minutes,

(b) separating by fractional distillation from the reaction product of step (a) said hydrocarbon composition containing from about 64 to about 85 weight percent dialkylbenzenes and from about 8 to about 25 weight percent alkyl-substituted tetrahydronaphthalenes.

19. The process of claim 18 wherein the reaction temperature of step (a) is from about 75 to about 120° C.

20. The process of claim 19 wherein the catalyst is aluminum chloride and the amount of catalyst is from about 0.5 to about 3 weight percent.

21. The process of claim 20 wherein the reaction temperature is about 100° C.

22. The product prepared by the process of claim 1.

23. The product prepared by the process of claim 13.

24. The product prepared by the process of claim 20.

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U.S. Cl. X.R.

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