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3,115,530

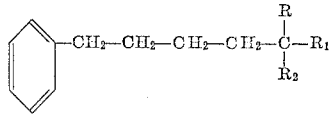
PREFERRED ALKYL ARYL SULFONATE DETERGENTS

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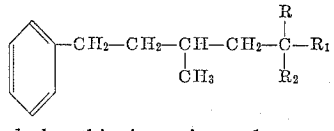
No Drawing. Filed May 13, 1960, Ser. No. 28,835
4 Claims. (Cl. 260—668)

This invention is concerned with new alkyl benzene hydrocarbons which are useful in the production of superior synthetic detergents, and with the preparation of these hydrocarbons. More particularly, this invention is concerned with the production of alkyl benzene hydrocarbons having at least one nuclear substituted alkyl chain containing from 8 to 17 carbon atoms, said alkyl chain having the structure of a normal tetramethylene or perhydroprenyl group attached between the benzene nucleus and a branched alkyl group. Illustrated in chemical notation, the new alkyl benzene hydrocarbons of this invention may be represented graphically by the following general formulae wherein R, R_1 and R_2 are acyclic branched or straight chain alkyl groups:

(I)



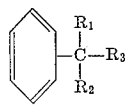
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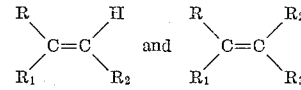
Most particularly, this invention relates to monoalkyl benzene hydrocarbons of the above described structure in which the tetramethylene moiety in the alkyl group of Formula I is derived from butadiene and the perhydroprenyl moiety of the alkyl group in Formula II is derived from isoprene. The sum of the carbon atoms in the alkyl groups R, R_1 and R_2 may vary from 3 to 11. This application is a C.I.P. of U.S. Serial No. 17,796, filed March 28, 1960.

The alkali metal sulfonate salts of these alkyl benzene hydrocarbons have now been found to be highly superior to other similar type detergents known in the prior art. This is true not only with respect to the washing properties of these detergents but also with respect to their capacity to be removed in conventional sewage disposal plants. Thus, the present detergents have been found to be substantially entirely absent from the effluent from such a sewage treating plant, having been removed by biodegradation, adsorption, and the like. This property is an extremely important factor in preventing the foaming which has been encountered in rivers and streams into which the effluent from sewage disposal plants is discharged. It should be noted that it is surprising that both of these improvements are obtained at the same time by utilizing the present easily and cheaply prepared materials having molecular structures as above described.

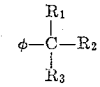
The present invention will be more clearly understood from a consideration of prior art commercial detergent materials made by alkylating benzene with polymers of propylene containing from 10 to 15 carbon atoms. These prior art detergent materials are the major ones used in the household detergents marketed today. These materials may be represented by the following chemical formula:



wherein R_1, R_2 and R_3 may be hydrogen, methyl, ethyl, isopropyl or higher straight or branched chain alkyl radicals, the sum of R_1, R_2 and R_3 averaging as previously mentioned 9 to 14 carbon atoms. The propylene polymer, for example, commercial tetrapropylene made by the catalytic polymerization of refinery C_3 streams over phosphoric acid on kieselguhr catalysts is known to consist predominantly of tri and tetra alkyl substituted ethylene



Thus, the alkyl aromatics obtained on alkylating benzene with this material possess in large part a trialkyl substituted carbon atom adjacent and attached to the aromatic nucleus, i.e.



wherein R_1, R_2 and R_3 are alkyl groups.

It is now known that these conventional commercial alkyl benzene sulfonates having a trialkyl substituted carbon atom attached to the aromatic ring are particularly resistant to biological degradation by bacteria normally present in micro-organism populations of activated sewage sludge (and that they are not otherwise removed by adsorption, etc.). Thus, it is known that severe foaming and frothing have occurred in rivers and streams into which sewage disposal plants discharge their effluent. It has now been found that the detergent material of the type described in this invention is readily removed by degradation or adsorption on the sludge and when processed in a sewage plant produces an effluent from said plant having little or no tendency to foam.

It has now been discovered that in addition to the superior biodegradable properties of the present detergents that these detergents also have superior washing properties. Thus, this superiority is obtained by utilizing a molecular structure wherein a normal tetramethylene group or perhydroprenyl group links the benzene ring to a branched alkyl material. Although it is not intended to limit this invention by a particular theory, this improvement in washing properties may be attributed to changing the molecular volume of the molecule by obtaining a proper balance in the length of the longest alkyl chain measured from its point of attachment to the methylene group. It should be noted that this object is not attained merely by utilizing a higher olefin such as pentapropylene or a higher fraction obtained from tetrapropylene as the alkylation feed as has been used in some commercial detergents. These detergents although superior in washing properties to conventional tetrapropylene obtained materials are still greatly inferior to the present invention detergents. Thus, it is theorized that just the right balance of solubility and emulsifying properties are obtained in the present product detergent.

A wide variety of methods may be used in preparing the new alkyl aromatics of the present invention. In all of these methods a branched material selected from the group consisting of polymers of propylene boiling in the tripropylene, tetrapropylene or tripropylene and tetrapropylene range and diisobutylene is:

(1) Reacted with a halogen acid,
(2) The resulting tertiary alkyl halide is reacted with butadiene or isoprene in the presence of a Friedel-Crafts catalyst,
(3) The condensation product formed is then reacted with benzene or a Grignard reagent derived from a halo

benzene such as phenyl magnesium chloride or a metallo derivative of a halo benzene such as phenyl lithium, and

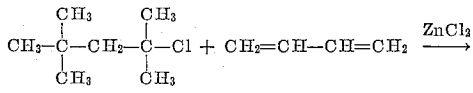
(4) The condensation product thus formed is hydrogenated to remove the unsaturation before sulfonation to the final active detergent composition.

In more detail the reactions utilized in the synthesis of the detergents are as follows. Propylene polymers suitable for use as feeds for the process may be obtained from a process as described in U.S. Patents 2,486,533 and 2,695,326. These patents describe processes wherein propylene is polymerized in the presence of phosphoric acid on kieselguhr catalyst to liquid polymers, herein termed U.O.P. polymers. A fraction of such polymers containing between 8 and 13 carbon atoms to the molecule may be used but preferably either a C_8 to C_{10} cut, predominantly C_9, or a C_{10} to C_{13} cut, predominantly C_{12}, is preferred. Isobutylene dimer also is a preferred feed stock in the present invention process. This latter material is prepared by extracting isobutylene from refinery C_4 streams with hot sulfuric acid so as to obtain both the desired separation and dimerization in the extract phase. Any of the above described feed stocks are then converted to the monohalide by reaction with a halogen acid, e.g. HCl at temperatures of −20 to 20° C., e.g. 0° C., and pressures of 1 to 5 atmospheres, e.g. 1.0 atmosphere.

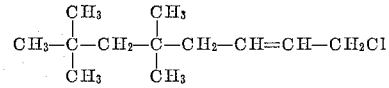
The resulting alkyl halides are then reacted with butadiene or isoprene in the presence of Friedel-Crafts catalyst at temperatures in the range of −10 to 100° C., preferably 15 to 50° C. The catalysts which are employed are the well known Friedel-Crafts type as typified by the halides of aluminum, titanium, antimony, bismuth, iron, boron, zinc and tin. Of these zinc chloride and stannic chloride are much preferred. The reaction is conveniently carried out in the presence of an inert organic solvent, although a solvent is not essential to the reaction. The word "inert" is used in the accepted sense as indicating that the solvent does not react with the reactants or products under the conditions of the instant reaction. Examples of suitable solvents include aliphatic hydrocarbons, such as pentane and hexane, and chlorinated aliphatic hydrocarbons, such as ethylene dichloride, carbon tetrachloride, or chloroform. While the butadiene or isoprene and the tertiary halide react in equimolar amounts, as much as a hundred percent excess of either reactant can be present.

The reactions of butadiene with the preferred feed stocks of this invention and products obtained therefrom are given below.

(I)



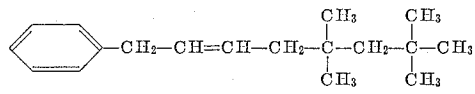
Diisobutene hydrochloride — Butadiene



1-chloro 5,5,7,7-tetramethyloctene-2

(II)

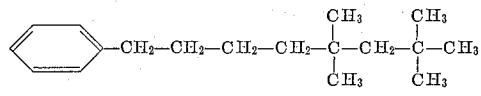
Tetramethyloctenylchloride + C_6H_5MgBr ⟶



1-phenyl 5,5,7,7-tetramethyloctene-2

(III)

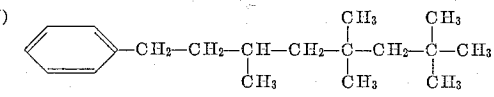
Phenyl, tetramethyl octene $\xrightarrow[Ni]{H_2}$



1-phenyl 5,5,7,7-tetramethyloctane

With diisobutylene and isoprene the chief product formed is:

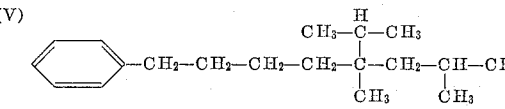
(IV)



2-phenyl 3,5,5,7,7-pentamethyloctane

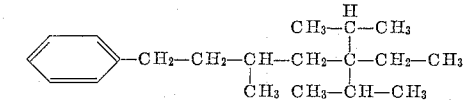
With tripropylene and butadiene the following product is obtained for illustration only (i.e. tripropylene is a mixture:

(V)



With tripropylene and isoprene there may be obtained for example:

(VI)



Following condensation the unsaturated halide is reacted at temperatures of −10 to 50° C., preferably 0 to 35° C., e.g. 20° C., with a Grignard reagent derived from a halobenzene such as phenyl magnesium bromide, or phenyl magnesium iodide, preferably phenyl magnesium chloride or a metallo derivative of a halo benzene such as preferably phenyl lithium although phenyl sodium also may be used. Mole ratios of aromatic material to unsaturated halide should be 1–1.2:1.

Alternatively the unsaturated halide may be reacted directly with benzene in the presence of a Friedel-Crafts type catalyst such as $AlCl_3$, $FeCl_3$, $SnCl_4$, BF_3, $ZnCl_2$, HF, H_2SO_4 (96%), P_2O_5, and H_3PO_4, preferably $AlCl_3$. Temperatures utilized may be in the range of 0 to 50° C., preferably 10 to 20° C., e.g. 15° C. Amounts of reactants and catalyst should be in the range of 2 to 10, preferably 3 to 6, e.g. 5, moles benzene per mole of unsaturated halide, and 0.1 to 1.0, e.g. .2, mole catalyst per mole of unsaturated halide.

The unsaturated alkyl benzene condensation product thus formed is then reacted with hydrogen at temperatures of 20 to 100° C., e.g. 35° C., in the presence of a hydrogenation catalyst such as platinum, palladium, or nickel alone or supported on a base such as alumina, e.g. platinum or alumina.

The alkyl benzenes are then sulfonated by conventional means to obtain the desired alkyl aryl sulfonic acids for detergents, e.g. by contact with an excess of concentrated acid, or fuming sulfuric acid or SO_3. The sulfonation may be carried out at temperatures up to 50° C. The acid concentration is preferably at least 98%. Acid up to 100% concentration and oleum, containing up to 20 wt. percent SO_3 or higher, may be employed. With higher acid concentration, lower reaction times are required, e.g. about 1 hour with 98% acid and ¼ hour with 20% oleum. Volume ratios of sulfuric acid to hydrocarbon may range from 0.8:1 to 1.25:1, a 1:1 ratio being suitable. The larger the ratio, the more inorganic sulfate will be present in the product, following neutralization. In many cases, the inorganic sulfate is a desirable constituent of the finished detergent composition.

The sulfonation product mixture is preferably freed, e.g., by water dilution and decanting, from excess sulfuric acid. The mixture is then neutralized, the sulfonic acids being thus converted to sulfonic acid salts and the excess sulfuric acid into sulfate. The neutralization may be carried out with any base or basic-reacting inorganic or organic substance. Thus, to produce sodium sulfonates, aqueous sodium hydroxide or sodium carbonates are suitably employed. Other alkali metal, alkaline earth metal, ammonium or amine salts may be similarly produced from the corresponding basic compounds. The neutralization is generally carried out by contact with

the aqueous solution at temperatures of from 20° to 100° C., those between 40 and 60° C., being preferred. Oil soluble or water soluble detergents may be obtained depending upon the distribution or amounts of the various chain lengths of the alkyl groups on the benzene ring and also on the average chain length of these alkyl groups.

Neither the methods used for preparation of the desired alkyl benzene hydrocarbons, nor the method for preparing the detergent materials described above, nor the examples which follow are to be construed as limiting the methods which are suitable for the preparation of these materials, since other methods for accomplishing the desired end as described are known in the art.

EXAMPLE I.—DODECYLBENZENE FROM DIISOBUTENE AND BUTADIENE

Part A.—Diisobutylene Hydrochloride

Two liters of freshly distilled diisobutylene consisting of a mixture of 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2 was saturated at 0 to 5° C. with gaseous hydrogen chloride. Absorption was slow at the beginning of the experiment, but addition of 0.5 ml. of water and 0.25 gm. of ferric chloride increased the absorption rate. When no further absorption was evident, the dissolved but unreacted HCl was swept from the reaction mixture with nitrogen and the product rapidly distilled under reduced pressure. Redistillation at 16 mm. Hg pressure thru a 15 plate Oldershaw column at 4:1 reflux ratio gave a pure product boiling at 47° C. It possesses the structure shown in Formula I, Column 3.

Part B

A one-liter glass lined reaction vessel previously cooled to 0° C. was charged with 297 grams of the tertiary octyl chloride prepared in Part A above, 108 grams of butadiene, 1 gram of tertiary butyl catechol inhibitor and 27 grams of finely ground, freshly-fused anhydrous zinc chloride. Air was purged from the system with nitrogen and the mixture was agitated in a thermostatically controlled water bath, under 10 p.s.i.g. nitrogen pressure at 20° C. for a period of 3 days. The crude product was filtered from a dark brown sludge, washed with water and dilute sodium carbonate and distilled at reduced pressure. There was obtained 215 grams of product boiling at 98 to 100° C. at 10 mm. pressure of Hg. It had the structure shown for the 1-chloro 5,5,7,7-tetramethyl octene-2 in Formula II.

Part C.—1-Phenyl-5,5,7,7-Tetramethyloctene-2

One hundred and fifty-seven grams of freshly distilled bromo benzene dissolved in 520 ml. of sodium-dried ether was slowly added under gentle reflux to 24.3 grams of magnesium turnings previously activated by warming with a crystal of iodine. After all the bromide had been added, stirring with reflux was continued for an additional 2 hours after which all of the magnesium had reacted. The mixture was then cooled to 10° C. and 202.5 grams of the dodecyl chloride prepared in Part B was slowly added. Temperature was controlled by cooling and after all of the chloride had been added the temperature was raised to reflux (41.5° C.) and heated under reflux for 3 hours. A heavy white precipitate formed.

The reaction mixture was decomposed with ice and 5% HCl, washed free of acid, dried, the ether removed on a steam bath and the crude product distilled under reduced pressure. There was obtained 220.5 grams of product boiling at 69 to 71° C. at 0.03 mm. pressure. Analysis showed the following:

	Found	Theoretical
Percent Carbon	88.6	88.45
Percent Hydrogen	11.4	11.55
Bromine No., eg./gm	65.0	65.40
Refractive Index 20° C./D	1.4980	

Part D.—1-Phenyl-5,5,7,7-Tetramethyl Octane

A hydrogenation bomb was charged with 150 grams of dodecenyl benzene prepared in Part C, 200 ml. of ethanol and 2.0 grams of 5% palladium on charcoal catalyst. Air was exhausted from the system and hydrogen charged at 40 p.s.i.g. Absorption of hydrogen was rapid with the temperature rising to 50° C. Hydrogen absorption stopped when nearly the theoretical quantity had been taken up. Crude product was filtered, alcohol removed and residue distilled under reduced pressure. There was obtained 141 grams of product boiling at 155 to 156° C. @ 10 mm. Analysis of the product showed the following:

	Found	Theoretical
Percent Carbon	87.80	87.73
Percent Hydrogen	12.21	12.27
Refractive Index 20° C./D	1.4890	

Mass spectrometer analysis:

	Percent
C_{10} benzene	0.15
C_{11} benzene	0.11
C_{12} benzene	99.76
C_{13} benzene	0.007

Part E.—Sodium 1-Phenyl-5,5,7,7-Tetramethyloctene-p-Sulfonate

Fifty grams of the dodecyl benzene prepared in Part D was sufonated with 70 grams of 20% oleum at 15 to 55° C., neutralized, desalted and crystallized twice from water. The para sulfonate is less soluble in water than the ortho sulfonate and may be separated by crystallization. The ortho sulfonate has a high solubility in water and is particularly adapted to the preparation of liquid detergents. Chemical analysis on the dried para sulfonate showed the following:

	Found	Theoretical
Percent Carbon	61.57	62.04
Percent Hydrogen	8.42	8.39
Percent Sulfur	9.26	9.20

Detergency evaluations are given below.

EXAMPLE II.—TRIDECYL BENZENE FROM DIISOBUTYLENE AND ISOPRENE

Diisobutylene hydrochloride prepared in Part A, Example I, was condensed with isoprene in the same manner as described in Part B of Example I. Tridecenyl chloride boiling at 85 to 90° C. at 3 mm. pressure was obtained. Analysis showed a chlorine content of 16.3 wt. percent compared to a theoretical content of 16.36. Condensation of the chloride with phenyl lithium prepared from bromo benzene and lithium metal gave a tridecenyl benzene boiling at 134 to 137° C. at 1.5 mm. pressure. Hydrogenation in the presence of palladium catalyst gave tridecyl benzene boiling at 140° C. at 1.3 mm. pressure. It sulfonated readily with 20% oleum to yield a snow-white detergent.

EXAMPLE III.—TRIDECYL BENZENE FROM TRIPROPYLENE AND BUTADIENE

Part A

Tripropylene, having a boiling point range of 133 to 140° C., made by the polymerization of propylene over U.O.P. catalyst was gassed with hydrogen chloride at 0 to 5° C. in the presence of water and ferric chloride in the same manner as diisobutylene hydrochloride was prepared in Part A, Example I. Distillation of the product

gave a fraction boiling at 60 to 80° C. at 20 mm. pressure. Analysis showed the following:

	Found	Theor. for $C_9H_{19}Cl$
Percent Carbon	69.70	66.44
Percent Hydrogen	12.20	11.77
Percent Chloride	18.18	21.79

The analysis corresponds closely with the known tertiary olefin content of commercial U.O.P. tripropylene.

Part B

Nonyl chloride prepared as in Part A, Example III, was condensed with butadiene using dichloromethane as solvent and a 5% solution of stannic chloride in the same solvent as catalyst. Distillation after reaction gave a tridecenyl chloride which on analysis showed it to be an allylic chloride. Condensation of this chloride with phenyl magnesium chloride gave a tridecenyl benzene which boiled at 147 to 152° C. at 1.2 mm. pressure. Hydrogenation of this product gave tridecyl benzene, boiling point 150 to 155° C. at 1.5 mm. pressure. Sulfonation of this product yielded a sodium sulfonate with outstanding detergency.

EXAMPLE IV.—DETERGENCY EVALUATION

A sample of the sodium dodecyl benzene sulfonate prepared as in Part E, Example I, above, was tested in comparison with a number of other detergents in a standard dishwashing test and cotton detergency test. The dishwashing test consisted in washing 8-inch white dinner plates, having 1.75 grams of a hydrogenated vegetable shortening distributed over the surface, in 6 liters of detergent solution made up with 2 or 8 grains hard water in a dishpan at 120° F.±1° F. at concentrations of 0.01 and 0.03 weight percent based on the active ingredient content until foam disappearance occurred. A trace of a colloidal dye, dispersed in the shortening, indicated lack of cleansing and the color disappears in the foam just before the end point. A conventional tetrapropyl benzene sulfonate was substituted for the sodium dodecyl benzene sulfonate and was tested for dishwashing in comparison with the product made in Example I, giving the results shown below in Table I.

TABLE I.—DISHWASHING TESTS

Product	Concentration/Hardness—Grains Per Gallon			
	.01/2	.03/2	.01/8	.03/8
Dodecyl Benzene, Part E, Example I, dishes	7	24	8	30
Commercial Tetrapropyl Benzene, dishes	3	20	6	22

EXAMPLE V

An additional amount of the sodium benzene sulfonate prepared as described above was tested in comparison with a number of other detergents in a standard cloth washing test. From the data obtained, presented below, it can be seen that again this material showed much improved results over the prior art tetrapropyl benzene commercial similarly built detergent material. In the table "U.S." stands for U.S. Testing Company, Dry Soiled Cloth; and "T.F." stands for Test Fabric, Inc., Oily Soiled Cloth.

TABLE II.—COTTON DETERGENCY—120° F.

Concentration / Water Hardness	0.03% 8 Grn.		0.05% 2 Grn.		0.05% 8 Grn.		0.1% 8 Grn.	
Soil Type	U.S.	T.F.	U.S.	T.F.	U.S.	T.F.	U.S.	T.F.
Sample ΔR [a]:								
Dodecylbenzene detergent	7.5	15.0	11.5	23.1	11.0	23.1	12.4	24.5
Commercial Sold "tetrapropyl" benzene detergents	6.1	12.7	9.7	15.5	9.9	15.0	10.3	16.4

[a] ΔR—Increase in percent reflectance after washing compared to unwashed, soiled cloth.

EXAMPLE VI.—BIOLOGICAL DEGRADATION

A sample of the sodium dodecyl benzene sulfonate prepared as described in Example I was tested in comparison with a commercial detergent sulfonate prepared by alkylating benzene with tetrapropylene (the commercial detergent having present also 19 weight percent of sodium sulfate and water). The equipment consisted of two banks of 4 glass columns each about 3 ft. high and 2 inches in diameter. The columns were packed with beds of Nottingham granite on which colonies of bacteria had been developed over a period of weeks. In each case a solution of the two detergents to be evaluated (about 1 liter of concentration 10 to 50 p.p.m.) together with a standard nutrient for the bacteria (malto-peptone) was added to each column and was circulated through the granite bed about seven times an hour. This type of "submerged digester" system is reasonably representative of the percolating filter type of commercial sewage plant, which according to government reports, is used at sewage works serving about 22 million of the population of the United Kingdom.

Samples were drawn from the columns after 15 minutes and after 1 hour, 2 hours and 24 hours. The quantity of detergent remaining in each sample was extracted with chloroform and the intensity of blue color developed with methylene blue was measured by a photoelectric absorptiometer in accordance with the standard method to obtain the percentage of detergent remaining in the sample.

The following data were obtained and are shown in the following table.

TABLE III

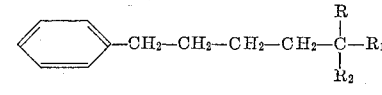
[Initial concentration, 50 p.p.m.]

Detergent	Initial Conc., p.p.m.	Wt. Percent Degraded After—			
		15 min.	1 hour	2 hours	24 hours
Sodium Dodecyl Benzene Sulfonate, Part E, Example I	50	40	60	70	93
Commercial Tetrapropyl Benzene Sulfonate (Containg also 19 wt. percent sodium sulfate and water)	50	17	31	34	38

It is to be understood that this invention is not limited to the specific examples, which have been offered merely as illustrations, and that modifications may be made without departing from the spirit of this invention.

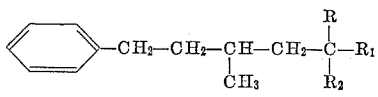
What is claimed is:

1.



wherein R, R_1 and R_2 are alkyl groups and wherein the total number of carbon atoms in the alkyl groups is in the range of 3 to 11.

2.



wherein R, R_1 and R_2 are alkyl groups and wherein the total number of carbon atoms in the alkyl groups is in the range of 3 to 11.

3. 1-phenyl-5,5,7,7-tetramethyl octane.

4. 1-phenyl-3,5,5,7,7-pentamethyl octane.

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