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3,196,174

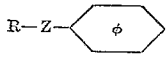
PERHYDRO BIS-(ISOPRENYL) ALKYL ARYL SULFONATES

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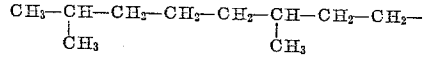
No Drawing. Filed Mar. 1, 1962, Ser. No. 176,802
5 Claims. (Cl. 260—505)

The present invention relates to new alkyl benzene hydrocarbons which are useful in the production of biodegradable synthetic detergents having highly superior washing properties. Further, this invention relates to the economic preparation of these hydrocarbons from inexpensive feed stocks. More particularly, this invention relates to the preparation of these hydrocarbons by reacting an aryl substituted alkyl alkali metal compound (preferably an arylalkyl lithium compound) under carefully chosen reaction conditions to obtain the selective growth of two moles of isoprene on to the aralkyl metal, hydrolyzing to obtain the corresponding alkadienyl benzene and hydrogenating to remove the unsaturation and thus produce the desired alkyl benzene material.

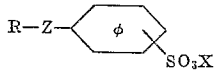
Illustrated in chemical notation the new alkyl benzene hydrocarbons of this invention may be represented by the following general formula.



wherein R is a perhydro bis (isoprenyl) alkyl radical containing ten carbon atoms comprising the structure



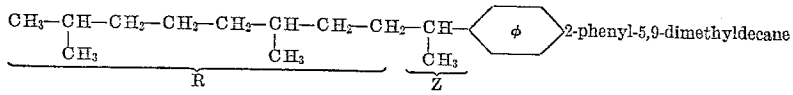
and Z is a two to four carbon atom alkylene group, the said alkylene group containing a single methyl group branch. The alkali metal sulfonate of these materials is represented by the following formula:



wherein X is an alkali metal, preferably sodium, and R and Z are as above described.

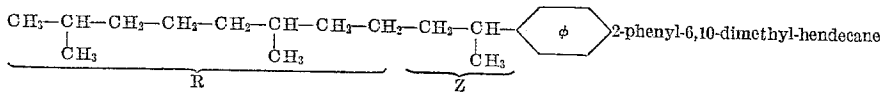
Illustrative examples of the hydrocarbon materials are:

(1)



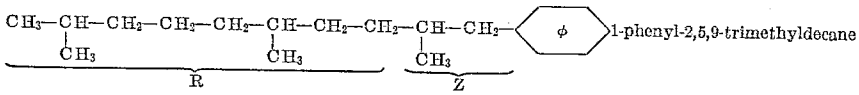
2-phenyl-5,9-dimethyldecane

(2)



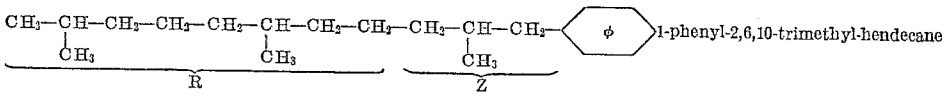
2-phenyl-6,10-dimethyl-hendecane

(3)



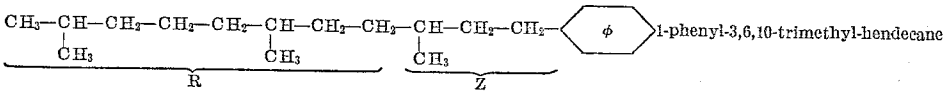
1-phenyl-2,5,9-trimethyldecane

(4)



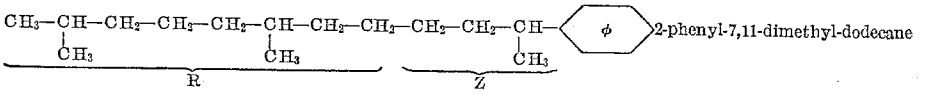
1-phenyl-2,6,10-trimethyl-hendecane

(5)



1-phenyl-3,6,10-trimethyl-hendecane

(6)



2-phenyl-7,11-dimethyl-dodecane

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, having been removed by biodegradation, adsorption, and the like. This property is an extremely important factor in preventing the foaming which has been encountered particularly in Europe 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.

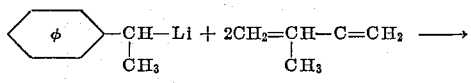
It is now known that conventional alkyl benzene sulfonates commercially prepared by alkylating benzene with tetrapropylene prepared by polymerizing propylene over a phosphoric acid on Kieselguhr catalyst are particularly resistant to biological degradation by bacteria normally present in microorganism populations of activated sewage sludge (and that they are not otherwise removed by adsorption, etc.). Further it is known that severe foaming and frothing have occurred in many locations where sewage disposal plants discharge their effluent into rivers and streams. It has now been found that the detergent materials of the type described in this invention are readily degraded biologically by the microorganisms normally present in this sludge or are otherwise removed so that when processed in a sewage plant the effluent from said plant has little or no tendency to foam.

It has now been surprisingly discovered that by the process of the present invention substantially fully biodegradable detergents are obtained and in addition these detergents possess substantially higher detersive power than conventional sodium sulfonates of tetrapropylbenzene. Thus, for example, at equal concentrations approximately twice the number of dishes can be washed with the new detergents herein described compared to a conventional tetrapropyl benzene sulfonate and brightness increases of the same order of magnitude are obtained in

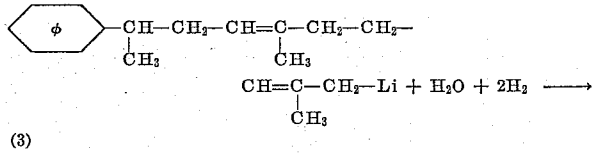
tests comparing the effectiveness of these detergents for soiled cotton cloth. Additionally, foaming power is exceptional without the use of the alkanolamides of fatty acids (foam builders) conventionally used in commercial detergents.

The present invention will be more clearly understood from a consideration of the general reaction sequence as applied to preparing one of the improved detergents of the present invention. Thus, two moles of isoprene are added to α ethyl phenyl lithium by growth reaction and the product material obtained after hydrolysis, is hydrogenated to obtain the desired saturated 2-phenyl-5,9-dimethyldecane as follows:

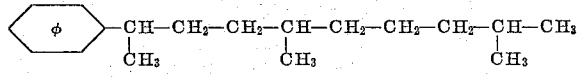
(1)



(2)



(3)



Alternatively, after the growth reaction the product (2) may be hydrogenated directly both to remove the Li by displacement and to saturate the double bonds.

The organolithium compounds having the general formula C_6H_5—Z—Li, where Z is a two to four carbon alkylene group having a single methyl branch may be prepared by the following general methods:

(1) By reaction of a suitable halogenated alkyl benzene with metallic lithium, preferably in a finely divided state and in the presence of a suitable solvent. Temperatures of below 0° C. to about 100° C. may be used depending on the nature of the halide or solvent and reaction times of from one to several hours may similarly vary.

$$C_6H_5—Z—X+2Li \rightarrow C_6H_5—Z—Li+LiX$$

(2) By reaction of a halogenated alkyl benzene with for example a lower alkyl lithium.

$$C_6H_5—Z—X+RLi \rightarrow C_6H_5—Z—Li+RX$$

(3) By reaction of an alkyl benzene with an alkyl lithium compound.

$$C_6H_5—Z—(H)+RLi \rightarrow C_6H_5—Z—Li+RH$$

(4) By addition of an alkyl lithium compound to an unsaturated alkyl benzene. ("—RH" below is "minus RH.")

$$C_6H_5—Z(—RH)+RLi \rightarrow C_6H_5—Z—Li$$

(5) By metal exchange with a Grignard compound prepared from a siutable halogenated alkyl benzene.

$$C_6H_5—Z—MgX+2Li \rightarrow C_6H_5—Z—Li+LiX+Mg$$

The preparation of organolithium compounds by the methods shown above and by other means is well known in the art and is not considered as a novel aspect of this invention.

Following the preparation of the aralkyl lithium compound this material is reacted with isoprene at pressures of from one to several hundred atmospheres, preferably one to ten atmospheres, e.g. 1 to 3 atmospheres, and at temperatures of below 0° C. to 100° C., preferably 0° C. to 50° C., e.g. 25° C. for times of 0.25–25 hours, preferably 1–12 hours, e.g. 3–4 hours. The amount of isoprene added is equal to 0.8 to 4 mols, preferably 1 to 3 mols, e.g. 2 mols of isoprene per mol of metal alkyl aryl. Thus, the desired aralkadienyl metal having e.g. two mols of isoprene added is obtained.

Following the growth reaction the product is hydrolyzed with water at temperautres of e.g. 0 to 100° C. to obtain the desired alkadienyl benzene. This hydrolysis may be carried out with or without an alcohol being present. If the alcohol is used, it may be added prior to the water hydrolysis. This makes the water hydrolysis less vigorous. Suitable alcohols are methanol, ethanol, isopropanol and the like. In any case considerable heat is evolved in the preliminary hydrolysis or alcoholysis and so rather large cooling capaicty is needed.

The alkadienyl benzene is then hydrogenated by conventional means. For example, this material may be contacted with two to one hundred moles of hydrogen per mole of unsaturated compound at temperatures of 25° C. to 125° C. and pressures of one to two thousand p.s.i.g. and in the presence of any of the hydrogenation catalysts well known to the art. Suitable catalysts are platinum, palladium and nickel, either as such or supported on a carrier. Of these the preferred catalyst is Raney nickel. Alternatively, as previously mentioned hydrogenation of the metal alkadienyl benzene compounds directly to the desired alkyl benzenes with recovery of the metal hydride for reuse can be obtained using the above described conditions. When the hydrogenation is completed, the product may be recovered by filtration from the catalyst and purified by distillation. It may be further purified prior to sulfonation by mild acid and clay treatment as disclosed in U.S. Patent 2,688,633.

The new alkyl benzenes may be sulfonated in known manner, e.g. by contact with an excess of concentrated sulfuric acid, oleum, $ClSO_3H$, sulfur trioxide, etc. The sulfonation may be carried out at temperatures up to 60° C., preferably for oleum 15° C. to 60° C., e.g. 40° C. The acid concentration is preferably at least 98%. Acid of 100% concentration and preferably oleum, containing up to e.g. 20 wt. percent SO_3 or higher, may be employed. With higher acid concentration, lower reaction times are required, e.g. about 3 to 4 hours with 98% acid, about 2 hours with 100% acid, and preferably 0.5 to 1 hour, e.g. 0.7 hour, with oleum. Weight ratios of sulfuric acid to hydrocarbon may range from 0.8:1 to 2.0:1, a 1.4:1 ratio being suitable when using 20% oleum, for example. 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.

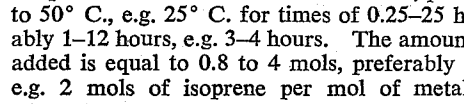
The sulfonation product mixture may be separated by "layering" with the addition of a limited amount of water to remove part of the excess spent acid before neutralizing or may be neutralized directly. When neutralized, the sulfonic acids are thus converted to sulfonic acid salts and the excess sulfuric 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 basic aqueous solution at temperatures of from 20° C. to 70° C., those between 30° C. and 50° C., e.g. 50° C., being preferred.

The present invention will be more clearly understood from a consideration of the following examples.

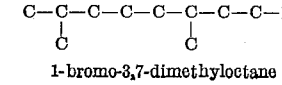
EXAMPLE I.—SYNTHESIS OF 2-PHENYL 5,9-DIMETHYLDECANE

2-phenyl 5,9-dimethyldecane was synthesized by the following series of steps.

(1)



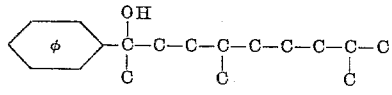
3,7-dimethyloctanol-1



1-bromo-3,7-dimethyloctane

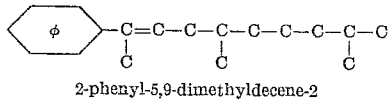
(2) (a) 1-bromo-3,7-dimethyloctane + Mg ⟶ Grignard

(b) Grignard + acetophenone ⟶



2-phenyl-5,9-dimethyldecanol-2

(3) 2-phenyl-5,9-dimethyldecanol-2 $\xrightarrow[60\%\ H_2SO_4]{-H_2O}$



2-phenyl-5,9-dimethyldecene-2

(4) 2-phenyl-5,9-dimethyldecene-2 $\xrightarrow[Pd]{H_2}$ 2-phenyl-5,9-dimethyldecane

(1) *1-bromo-3,7-dimethyloctane*

One mole (158 gms.) of 3,7-dimethyloctanol-1 (B.P. 114 C. @ 20 torr n^{20}/D 1.4369) made by the hydrogenation of citronellol over Raney nickel was reacted at −5 to 0° C. with 100 grams of PBr_3 followed by heating on a water bath at 70° C. for 2 hours. The mixture was then distilled rapidly at low pressure (1 mm.) to a pot temperature of 125° C. to obtain a distillate weighing 177 gms. and a residue ($P(OH)_3$) of 50 grams. The distillate was extracted twice with 50 ml. portions of ice-cold 96% H_2SO_4, neutralized with NH_4OH and extracted with methanol. The product was dried over K_2CO_3 and distilled at reduced pressure. B.P. 44–45° C. @ 0.4 torr. Yield 156 grams=70%.

(2) *2-phenyl-2-hydroxy-5,9-dimethyldecane*

155 grams (0.7 mole) of the above bromide was Grignardized with 28.5 grams (1.17 moles) of magnesium which had been activated with iodine using a total of 550 ml. of ether. After initial reaction the mixture was heated under reflux for 2 hours. 84 grams (0.70 mole) of acetophenone were added at 15° C. with stirring and the mixture was then heated under reflux for 4 hours. The Grignard product was decomposed with HCl, extracted and distilled under high vacuum. B.P. 113–116° C. @ 1.0 torr. Yield 136 gm.

(3) *2-phenyl-5,9-dimethyldecene-2*

136 gm. of the phenyl hydroxy decane was dehydrated by refluxing with 500 ml. of 60 wt. percent H_2SO_4 for 4 hours. After isolation the product was distilled under vacuum using a spinning band column. B.P. 143° C. @ 4 torr. Yield 105 gm.

(4) *2-phenyl-5,9-dimehtyldecane*

100 gms. of the olefin was dissolved in 200 ml. of anhydrous ethanol and hydrogenated with the aid of 1.0 gram of 5% palladium on charcoal at a pressure of 40 p.s.i.g. for 4 hours.

Distillation at 5:1 reflux ratio through a spinning band column yielded 86 gms. of product. B.P. 140–141 @ 3.9–4.0 torr. *n* 20/D 1.4813.

Analysis.—Found: C=87.77, H=12.24. theor.: C=87.73, H=12.27.

EXAMPLE II.—2-PHENYL 6,10-DIMETHYLHENDECANE

(1) *2,6-dimethylhendecanone-2*

Pseudoionone, (2,6-dimethylhendeca-2,6,8-triene-10-one) made by the condensation of citral with acetone was hydrogenated at 40 p.s.i.g. and 40° C. over a palladium on charcoal catalyst until three moles of hydrogen had been absorbed. Distillation under a spinning-band column gave a pure product showing no unsaturation by infrared spectroscopy. B.P. 118° C. @ 12 torr. *n* 20/D 1.4345.

(2) *2-phenyl 6,10-dimethylhendecanol-2*

A Grignard reagent prepared from 173 grams bromobenzene in 500 ml. anhydrous ether and 40 grams of magnesium turnings in 100 ml. ether was reacted with 198 grams of perhydroseudoionone at 5° C. The reaction mixture was then heated under reflux for 3 hours. The reaction products were decomposed with ice and HCl and after removing solvent, distilled under reduced pressure. B.P. 135° C. @ 1.2 torr. Wt. 245 gms. *n* 20/D=1.4972.

(3) *2-phenyl 6,10-dimethylhendecene-2*

The above carbinol was dehydrated by heating with 500 ml. of 60% sufuric acid at 100° C. for 4 hours. The reaction product was isolated and distilled at reduced pressure. B.P. 97–98° C. @ 0.025 torr. Wt. 211 gms. *n* 20/D=1.5029.

(4) *2-phenyl 6,10-dimethlyhendecane*

The above prepared olefin was reduced at 40 p.s.i.g. over a Pd catalyst. The product was fractionated through a spinning-band column. B.P. 87–88° C. @ 0.025 torr. Wt.=189 gms. *n* 20/D=1.4807.

EXAMPLE III.—1-PHENYL-2,6,10-TRIMETHYL-HENDECANE

This alkyl benzene was prepared in the same manner as the product of Example II, except that benzyl chloride was used instead of bromo benzene.

(1) *1-phenyl 2,6,10-trimethylhendecane-2*

The above product was prepared by reacting a Grignard consisting of 18 gm. magnesium, 73 grams benzyl chloride and 200 ml. ether with 96 grams perhydroseudoionone. The crude produce was stripped to 170° C. @ 1 torr. without distillation. Wt.=1.34.4 grams.

(2) *1-phenyl 2,6,10-trimethylhendecene-2*

The crude product prepared above was dehydrated at 100° C. for 4 hours with 500 grams of 60% H_2SO_4. B.P. 108–110° C. @ 0.08 torr. Wt.=106.4 gms. *n* 20/*d*=1.4950.

(3) *1-phenyl 2,6,10-trimethylhendecane*

The above prepared olefin diluted with 250 ml. of absolute ethanol was hydrogenated at 45° C. and 40 p.s.i.g. over 2 grams of 5% Pd on charcoal. B.P. 105–160 C. @ 0.07 torr. Wt.=91 gms. *n* 20/D=1.4872.

EXAMPLE IV.—1-PHENYL 2,5,9-TRIMETHYLDECANE

This hydrocarbon is prepared in similar manner to the product of Example I from 1-phenyl propanone-2 and a Grignard prepared from 1-bromo 3,7-dimethyloctane.

EXAMPLE V.—1-PHENYL 3,6,10-TRIMETHYLHENDECANE

This hydrocarbon is prepared in similar manner to the product of Example I from 1-phenyl butanone-3 and a Grignard prepared from 1-bromo 3,7-dimethyloctane.

EXAMPLE VI.—2-PHENYL 7,11-DIMETHYLDODECANE

This hydrocarbon is prepared in similar manner to the product of Example I from 3-phenyl butyraldehyde and a Grignard prepared from 1-bromo 3,7-dimethyloctane.

A number of the alkyl benzenes prepared above were checked for purity by means of capillary gas chromatography. Analytical data obtained by this means are more precise than a simple carbon and hydrogen analysis. Through the use of two internal standards, namely; benzene and hexadecane, relative retention times were obtained for a number of products. Retention times under the conditions noted below were calculated on the basis of benzene equal to zero and hexadecane equal to 1.00.

CAPILLARY GAS CHROMATOGRAPHY

Instrument	Barber-Colman.
Column	150 ft. capillary.
Coating	Apeizon–L.
Flash heater	213°C.
Column heater	200° C.
Cell temp.	215° C.
Ionization source	Strontium–90.
Carrier gas	Argon—20 p.s.i.g.
Voltage	1250.

Product:	Retention time
1-phenyl dodecane	3.75
2-phenyl dodecane	2.56
3-phenyldodecane	2.12
4-phenyldodecane	1.87
5-phenyldodecane	1.75
6-phenyldodecane	1.69
2-phenyl 5,9-dimethyldecane	1.54
2-phenyl 6,10-dimethylhendecane	2.38
1-phenyl 2,6,10-trimethylhendecane	3.92
1-phenyl 6-cyclohexylhexane	5.55
1-phenyl 5,5,7,7-tetramethyloctane	1.94

EXAMPLE VII

Fifty grams of the alkyl benzenes prepared as in the above examples were sulfonated with seventy grams of 20% oleum at a maximum temperature of 55° C. for a total contact time of one-half hour. Following neutralization with sodium hydroxide, the products were deoiled by extraction with petroleum ether and desalted by dehydration with excess sodium carbonate from a solution in isopropyl alcohol. Evaporation to dryness under vacuum gave pure dry sulfonates.

EXAMPLE VIII

A number of the sulfonates prepared above were tested in a standard dishwashing procedure at a concentration of 0.03% of pure detergent in 8 grain water at a temperature of 120° F. and compared with a standard tetrapropylbenzene sulfonate.

Product:	Dishes washed
Sod. sulfonate 2-phenyldodecane	16
Sod. sulfonate 2-phenyl 5,9-dimethyldecane	31
Sod. sulfonate 2-phenyl 6,10-dimethylhendecane	29
Sod. sulfonate tetrapropylbenzene	15

EXAMPLE IX

Cotton detergency using standard soiled cloth was determined for a number of sulfonates in a build formulation. All products were tested at 0.15 and 0.25% at 120° F. in 8 grain water of the built formulation using the following composition.

	Wt. percent
Test sod. alkyl benzene sulfonate	20
Sodium tripolyphosphate	30
Tetrasodium pyrophosphate	10
Sodium metasilicate	5
Sodium carboxymethyl cellulose	1
Sodium sulfate	34

Cotton Detergency

Concentration (100% Active) [1]	Increase in Reflectance			
	0.03%		0.05%	
Cotton-Soil Type [2]	U.S.	T.F.	U.S.	T.F.
2-Phenyldodecane	9.8	15.2	10.6	15.7
2-Phenyl 5,9-Dimethyldecane	13.9	16.8	14.5	19.0
2-Phenyl 6,10-Dimethylhendecane	13.9	18.0	16.1	19.3
1-Phenyl 2,6,10-Trimethylhendecane	15.5	18.8	17.0	19.4
Standard Tetrapropylbenzene	4.9	10.3	10.0	12.4

[1] Samples tested at 0.15 and 0.25% concentration in 8 grain hard water at 120° F. in Terg-O-Tometer in a built formulation containing 20% active ingredient.
[2] U.S.=United States Testing Co. dry-carbon-soil on Indian Head Cotton. T.F.=Test Fabrics Co. oily-carbon-soil on 80 square print cotton.

EXAMPLE X.—BIODEGRADATION

Two types of tests were employed for determining the biodegradability of the synthetic detergents prepared according to this invention.

In an "Activated Sludge Test," fifty milligrams of the detergent along with one liter of synthetic sewage was fed daily to aeration units containing approximately 2000 milligrams of activated sludge per liter. Effluent from the unit was removed daily and the residual detergent determined by means of methylene-blue and the foaming characteristics determined by blowing a fixed rate of air through a standard volume of effluent. Details of this test have been published by J. F. Nelson et al., "Developments in Industrial Microbiology" Plenum Press, New York, 1961.

In a "Simulated River Water" test the sewage organisms were acclimated to the detergent for a period of about 2 months and then "starved" so that the only source of food was the synthetic detergent.

The results obtained with these tests are shown below.

ACTIVATED SLUDGE TEST

	Percent Disappearance [1]			Foam Height [2]		
Days on Test	8	16	20	Orig.	16	20
2-Phenyldodecane	100	99	100	16	0	0
Example I	92	95	95	17.5	2	3
Example II	94	95	96	16	2	2
Tetrapropylbenzene	8	6	4	14	14	14

[1] By Methylene-Blue Test.
[2] Foam height in cm.

Sodium sulfonates of above alkylbenzenes tested at 50 mgm. per Liter.

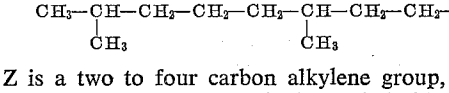
SIMULATED RIVER TEST

	Percent Disappearance [2]	
Days on Test [1]	26	56
Sod. Sulf. 2-Phenyldodecane	100	100
Sod. Sulf. Example I	95	93
Sod. Sulf. Example II	96	95
Sod. Sulf. Tetrapropylbenzene	0	4

[1] After initial acclimation.
[2] By Methylene-Blue.

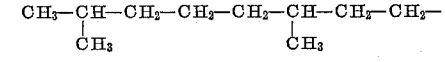
What is claimed is:

1. The composition of matter R—Z—C_6H_4—SO_3H which is the sulfonation product of the compound R—Z—C_6H_5 and wherein R is a perhydro bis-(isoprenyl) alkyl radical having predominantly the structure



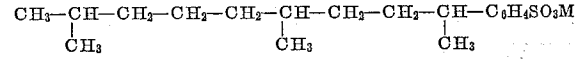
and Z is a two to four carbon alkylene group, the said alkylene group containing a single methyl side chain.

2. The composition of matter R—Z—C_6H_4—SO_3M which is the sulfonation product of the compound R—Z—C_6H_5 and wherein R is a perhydro bis-(isoprenyl) alkyl radical having predominantly the structure

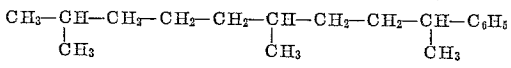


Z is a two to four carbon alkylene group, the said alkylene group containing a single methyl side chain, and M is an alkali metal.

3. The composition of matter

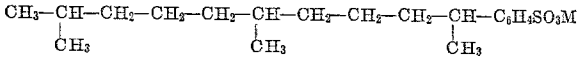


which is the sulfonation product of the compound

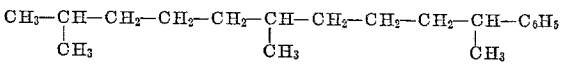


wherein M is an alkali metal.

4. The composition of matter

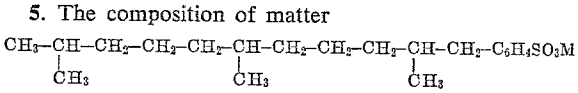


which is the sulfonation product of the compound

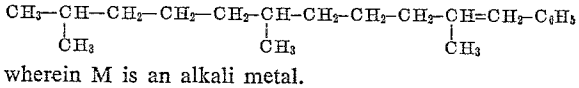


wherein M is an alkali metal.

5. The composition of matter



which is the sulfonation product of the compound



wherein M is an alkali metal.

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