

THE PREPARATION OF MODEL LONG CHAIN ALKYL BENZENES AND A STUDY OF THEIR ISOMERIC SULFONATION PRODUCTS

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Commercial sodium dodecylbenzenesulfonates widely used in detergent compositions are obtained by alkylating benzene with polypropylene averaging about the tetramer, sulfonating the alkylaryl hydrocarbon with sulfuric acid, oleum, or sulfur trioxide and neutralizing the sulfonic acid mix with sodium hydroxide. The side chain structure of the hydrocarbon and the distribution of the possible sulfonate isomers are essentially unknown.

Although long chain phenylalkanes of known structure have been synthesized and sulfonated, the possibility of ring isomerism in the sulfonate and its effect on the surface active characteristics have not been previously considered. The objective of the present series of investigations is to synthesize phenylalkanes by unequivocal means, sulfonate these hydrocarbons, isolate the sulfonate isomers and examine their physical and chemical properties. This paper reports the preparation and sulfonation of 1-phenyloctane, 1-phenyldodecane, 2-phenyltridecane, and 5-phenyldodecane. The surface active properties of detergency, foam, wetting and surface tension of the isolated *ortho* and *para* sulfonates have been studied in order to obtain a measure of the effect of the differences between these isomers in relation to the position of the phenyl group in the long aliphatic chain.

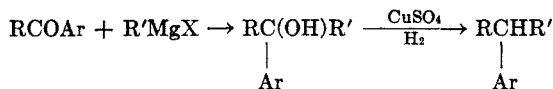
The synthesis of 1-phenyloctane and 1-phenyldodecane by the following sequence of reactions gave the desired products in good yield:



In the course of the preparation of these compounds studies were made to determine the most efficient and satisfactory laboratory procedure for the reduction of the ketones. Paquette, Lingafelter, and Tartar (1) prepared these hydrocarbons by the above sequence of reactions with the exception that a Clemmensen reduction was used with the respective ketones. We tried the modified Clemmensen procedure described by Martin (2) with *n*-undecyl phenyl ketone but obtained no significant increase in yield over that obtained by the regular Clemmensen method. Upon hydrogenating *n*-undecyl phenyl ketone at slightly higher than atmospheric pressure under the catalytic conditions employed by Ju, Shen, and Wood (3) we encountered the same difficulties of sluggish hydrogenation experienced by them. By use of the Huang-Minlon (4) modification of the Wolff-Kishner reaction the desired hydrocarbons were obtained in good quality and yield.

The 2-phenyltridecane and 5-phenyldodecane were prepared by conversion of *n*-undecyl phenyl ketone and *n*-heptyl phenyl ketone to tertiary alcohols by

means of Grignard reagents. The resulting alcohols were dehydrated to the alkenes which were catalytically hydrogenated to the desired products.



where $\text{R}' = \text{CH}_3$; $\text{R} = \text{C}_{11}\text{H}_{23}$

where $\text{R}' = \text{C}_4\text{H}_9$; $\text{R} = \text{C}_7\text{H}_{15}$

The infrared spectra of the phenylalkanes are presented in Figure 1. The spectra of 1-phenyloctane and 1-phenyldodecane are identical with those previously published by the American Petroleum Institute (5) but 1-phenyldodecane is shown here for purposes of comparison. The 1-phenyloctane and 1-phenyldodecane as illustrated by the latter hydrocarbon (Fig. 1A) have 3 significant absorption bands at 13.45, 13.85, and 14.36 μ in the region of 13–15 μ . In the same region, 2-phenyltridecane (Fig. 1B) has absorption bands at 13.15, 13.88, and 14.32 μ . Recently, Lenneman, Hites, and Komarewsky (6) investigated the alkylation of benzene with high molecular weight 1-alkenes and from infrared data concluded the compounds to be all 2-phenylalkanes. They eliminated the possibility of 4-, 5-, 6-, or 7-phenylalkanes on the basis that these compounds

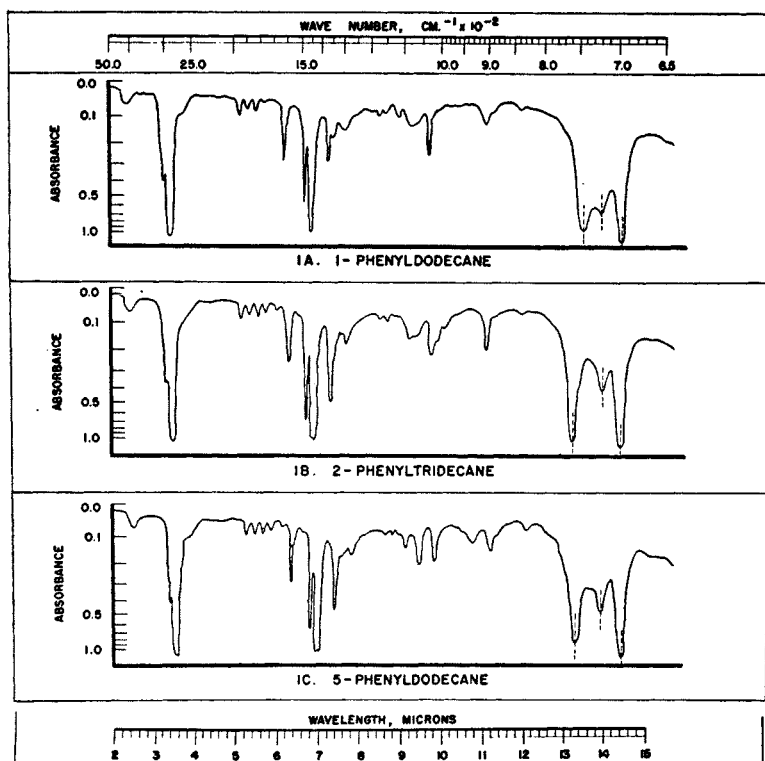


FIG. 1. INFRARED SPECTRA OF ALKYL BENZENES (0.025-mm. cell)

would be expected, due to the presence of two methylene chains of different lengths, to produce two absorption bands in the 13.40 to 13.90 μ region. Although it is true that the spectra of their compounds have a marked similarity with the spectrum of our 2-phenyltridecane, the exclusion of the 4-, 5-, 6-, or 7-isomers appears questionable since their expected absorption bands at 13.40 to 13.90 μ are absent in the spectrum (Fig. 1C) of our 5-phenyldodecane. It may be observed that a marked difference exists in the 13–15 μ region between the spectra of those phenyl alkanes in which the phenyl group is attached to a carbon atom possessing one as compared to two alkyl groups. Differences between isomers of the latter type are much less marked, and therefore their differentiation by infrared analyses requires careful scrutiny.

The sulfonation of high molecular weight phenylalkanes has been reported by previous workers (1, 7, 8) but the isomer distribution of the sulfonates has not been established. Paquette, *et al.* (1) were able to separate and purify some sodium *p*-octylbenzenesulfonate and sodium *p*-dodecylbenzenesulfonate (38% yield) by several crystallizations from alcohol. A second isomer was observed in both cases during purification process but attempts to separate it from the *para* isomer by crystallization from alcohol were unsuccessful.

An elegant synthesis of the isomeric dodecylbenzenesulfonates was carried out by Truce and Lyons (9). The synthesis involves the treatment of the dialkylcadmium compound, prepared from *n*-undecylmagnesium bromide with the appropriate bromobenzoyl chloride in order to produce, upon hydrogenation, the desired alkylaryl bromide isomer intermediates. Conversion of the bromides to the corresponding sodium *o*-, *m*-, or *p*-sulfonates in yields of 16, 35, and 45% respectively, based on the intermediate used, was accomplished by preparing the aryllithium compounds, sulfinating them, and then oxidizing the sulfinic acids to the sulfonates. These compounds were characterized as the S-benzylthiuronium salts, the melting points of which were valuable along with infrared spectra for determining the isomer distribution in our sulfonation studies.

On sulfonation of the hydrocarbons, 1-phenyloctane and 1-phenyldodecane

TABLE I
S-BENZYLTHIURONIUM SALTS OF ISOMERIC ALKYL BENZENESULFONATES

R' RCHC ₆ H ₄ SO ₂ Na		R	m.p., ^a °C. (<i>found</i>)	m.p., °C. (<i>ref. 9</i>)	Nitrogen		Sulfur	
Orientation	R'				Calc'd	Found	Calc'd	Found
<i>p</i>	H	C ₁₁ H ₂₃	117–118	117–118	5.68	5.78	12.99	13.02
<i>o</i>	H	C ₁₁ H ₂₃	101–103	100–101	5.68	5.83	12.99	12.97
<i>m</i>	H	C ₁₁ H ₂₃	92–94	97–98	—	—	—	—
<i>p</i>	H	C ₇ H ₁₅	125.5–126	—	6.42	6.75	14.66	14.52
<i>o</i>	H	C ₇ H ₁₅	105.5–106	—	6.42	6.41	14.66	14.52
<i>p</i>	CH ₃	C ₁₁ H ₂₃	105–106	—	5.53	5.57	12.63	12.70
<i>p</i>	C ₄ H ₉	C ₇ H ₁₅	140	—	5.68	5.77	12.99	13.03

^a All melting points were taken after drying at least six hours over P₂O₅ at 78° (2 mm.).

with 20% oleum followed by neutralization with sodium hydroxide we were able to isolate sodium *p*-octylbenzenesulfonate and sodium *p*-dodecylbenzenesulfonate in approximately 70% and 80% yields respectively. In order to ascertain whether the sulfonate isomer distribution would change with sulfur trioxide as the sulfonating agent, we sulfonated 1-phenyldodecane with this reagent in the vapor phase. After neutralization and separation, approximately the same ratio of *para* or *ortho* was obtained as with 20% oleum.

The low solubility of sodium *p*-octylbenzenesulfonate and sodium *p*-dodecylbenzenesulfonate in water at room temperature affords a means of separation from inorganic salt, *ortho* isomer, and other contaminants. The *ortho* isomers contained in the aqueous filtrates from the *para* isomers were isolated by extraction and purified by crystallization.

From a large scale laboratory sulfonation of 1-phenyldodecane (10) there was isolated less than 1% of material that appears by infrared analysis (Fig. 2C) to be the *meta* isomer.

The sodium *o*-octylbenzenesulfonate and the sodium *o*-dodecylbenzenesulfonate differ in physical properties from their respective *para* isomers. Whereas the *para* isomers are crystalline non-tacky products with low solubility in water or organic solvents, the *ortho* isomers are sticky, less crystalline compounds that are very soluble in polar or non-polar solvents.

The sulfonation of the hydrocarbons 2-phenyltridecane and 5-phenyldodecane with 20% oleum was conducted under the same conditions used for the above mentioned hydrocarbons. The sodium *p*-(1-methyldodecyl)benzenesulfonate (Fig. 2E) was isolated as a white crystalline compound. The aqueous filtrate contained the *ortho* isomer but the yield of this component was appreciably less than was found on sulfonation of the hydrocarbons having the phenyl group in the 1-position. In addition, separation from some admixed *para* and other impurities was much more difficult than purification of sodium *o*-dodecylbenzenesulfonate. Recrystallizations from acetone enriched the *ortho* content but infrared absorption showed that some *para* isomer was still present.

The infrared spectrum of the sulfonated product of 5-phenyldodecane indicates that it was predominately *para* isomer with a trace of *ortho* isomer present. Recrystallization from the minimum amount of acetone at low temperature gave an amorphous product which was shown (Fig. 2F) to be sodium *p*-(1-butyl-octyl)benzenesulfonate.

It is concluded from examination of the sulfonates obtained in this study that, as the position of the phenyl group is moved toward the center of a long alkyl chain, the yield of *ortho* isomer decreases. It is conceivable that steric hindrance may account for this decrease. In addition, as the phenyl group is moved toward the center of the chain the crystallinity of the *para* isomers decreases to yield products whose physical and chemical properties resemble those of the *ortho* isomers of alkylbenzenesulfonates having the phenyl group in a position near or at the end of the hydrocarbon chain. In regard to crystallinity it is interesting to note the similarity of these compounds to alkyl sulfates. When the sulfate group is located near the center of a long chain, the alkyl sulfates are

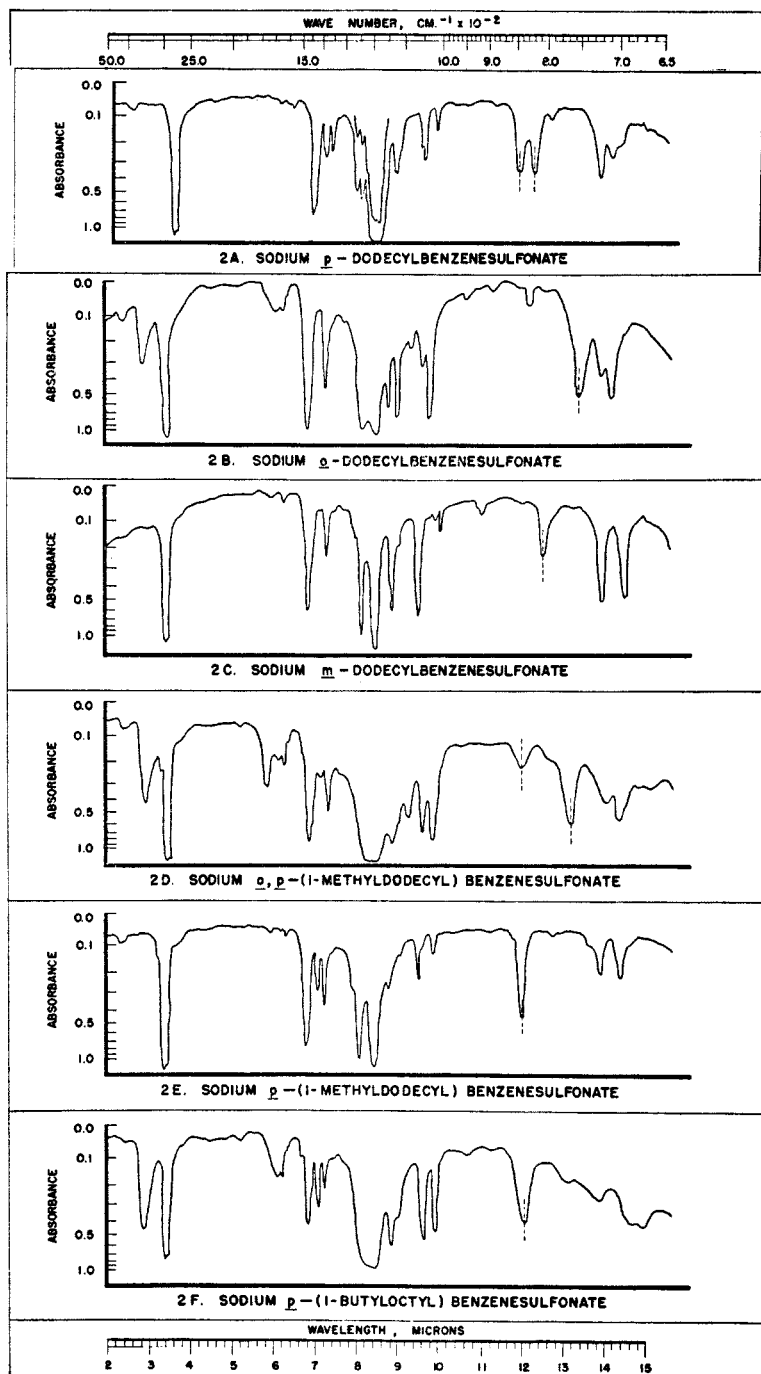


FIG. 2. INFRARED SPECTRA OF SODIUM ALKYL BENZENESULFONATES (NUJOL MULLS)

gelatinous in nature, whereas the isomers with this group located near or at the end of the chain are crystalline solids.

The sulfonate isomers were identified by means of the S-benzylthiuronium derivatives and infrared spectra. The S-benzylthiuronium salts of the *ortho* and *para* dodecylbenzenesulfonates correspond to those cited by Truce and Lyons (9) but the melting point of the *meta* isomer was slightly lower than that reported by these workers.

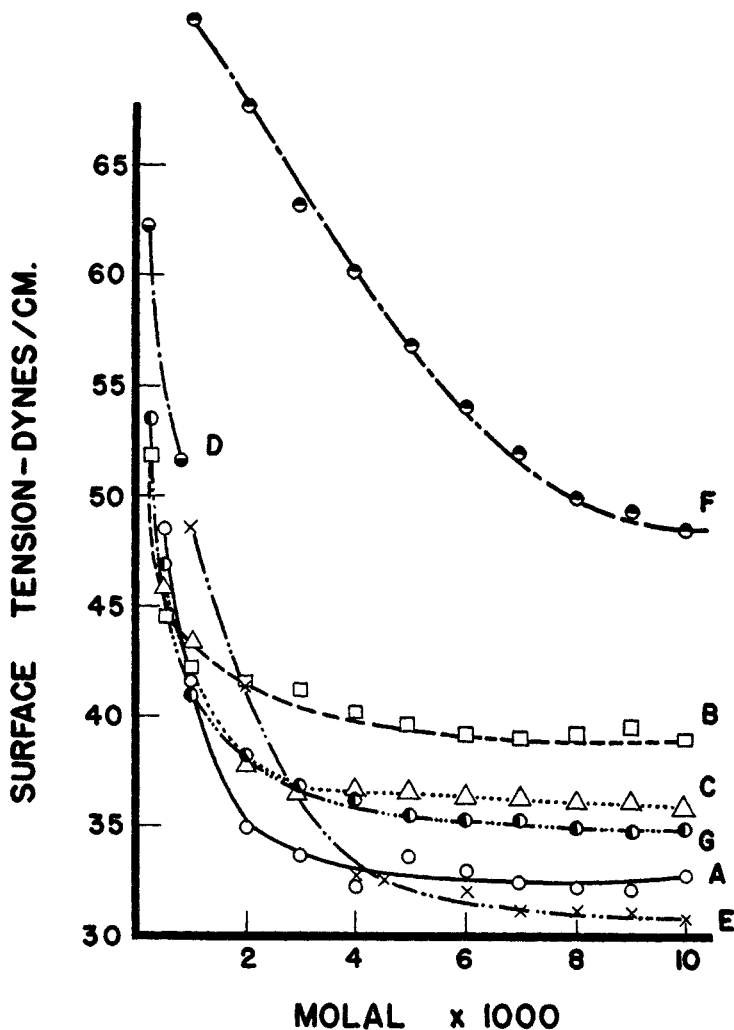


FIG. 3. SURFACE TENSION vs. CONCENTRATION FOR AQUEOUS SOLUTIONS OF SODIUM ALKYL-BENZENESULFONATES AT 25°.

- | | |
|---|---|
| A. Sodium <i>p</i> -(1-butyloctyl)benzenesulfonate | E. Sodium <i>o</i> -octylbenzenesulfonate |
| B. Sodium <i>p</i> -(1-methyldodecyl)benzenesulfonate | F. Sodium <i>p</i> -octylbenzenesulfonate |
| C. Sodium <i>o</i> -dodecylbenzenesulfonate | G. Sodium <i>o</i> -(1-methyldodecyl)benzenesulfonate |
| D. Sodium <i>p</i> -dodecylbenzenesulfonate | |

TABLE II
WETTING TIME OF SODIUM ALKYL BENZENESULFONATES

$\begin{array}{c} \text{R}' \\ \\ \text{RCHC}_6\text{H}_4\text{SO}_3\text{Na} \end{array}$			Wetting Time, seconds % concentration \times 1000 at 60°			
Orientation	R	R'	15	30	75	150
<i>p</i>	C ₁₁ H ₂₃	H	>300	>300	>300	>300
<i>o</i>	C ₁₁ H ₂₃	H	>300	>300	>300	32.6
<i>p</i>	C ₁₁ H ₂₃	CH ₃	>300	>300	155.6	25.2
<i>p</i>	C ₇ H ₁₅	C ₄ H ₉	>300	187	14.9	8.4
<i>p</i>	C ₇ H ₁₅	H	>300	>300	>300	>300
<i>o</i>	C ₇ H ₁₅	H	>300	>300	>300	103

The sodium *p*-, *o*-, and *m*-dodecylbenzenesulfonates (Figs. 2A, 2B, 2C) possess strong sulfonate absorption in the 8.08–8.52 μ region. The *ortho* isomer has a characteristic absorption at 13.36 μ , and the *meta* isomer at 12.50 μ , while the *para* isomer shows an absorption doublet at 11.90 and 12.28 μ .

The sodium *p*-(1-butyloctyl)benzenesulfonate (Fig. 2F) and the sodium *p*-(1-methyldodecyl)benzenesulfonate (Fig. 2E) show the expected sulfonate absorption in the 8.08–8.52 μ region. Instead of the doublet at 11.90, 12.28 μ observed for sodium *p*-dodecylbenzenesulfonate, these compounds exhibit a single *para* absorption at about 12.00 μ which may be attributed to the phenyl group being attached to a carbon atom bearing two alkyl groups.

The surface active behavior of long chain *ortho* and *para* sodium alkylbenzenesulfonates has not been compared previously. The surface tension concentration curves (Fig. 3) reveal significant structure effects due to sulfonate location on the benzene ring and the position of the phenyl group on the alkyl chain. Correlation between structure and surface activity was previously demonstrated by Hartley (11) in his work with alkoxy- and dialkoxy-benzenesulfonates. He observed that, by using compounds having two alkoxy groups rather than a single longer one, a lower limiting interfacial tension value is obtained at the higher concentrations presumably because of inhibition of micelle formation. Our surface tension data suggest that a similar relationship exists in regard to molecular configuration when the phenyl group is moved toward the center of a long alkyl chain or when the position of the sulfonate group is changed from *para* to *ortho* on the benzene ring.

Several years ago it was observed that sodium alkyl sulfates containing the sulfate group farther away from the end of a hydrocarbon chain exhibit better wetting as well as better foam stability (12). The comparative effect of the position of the sulfonate group is demonstrated by the *para* sulfonate obtained from 5-phenyldodecane being superior in wetting (Table II) and foaming properties (Fig. 4) to the *para* sulfonate obtained from 1-phenyldodecane. Also, the *ortho* sulfonates possess better wetting and equal or better foaming action than their respective *para* isomers. These differences in behavior probably are attributable

to structural configurations affecting micelle formation as evidenced by low surface tension in accordance with Hartley's theory.

The comparative detergency values of the alkylbenzenesulfonates are graphically presented in Fig. 5. It is apparent that under the specific detergency testing conditions, sodium octylbenzenesulfonate is a relatively poor detergent with no measurable difference detected for its sulfonate isomers. In contrast, sodium *p*-dodecylbenzenesulfonate is an excellent detergent and is far superior to its *ortho* isomer. Unfortunately, the limited quantity of *ortho* sulfonate derived by direct sulfonation of 2-phenyltridecane did not permit a comparison of its detergency ability with the *para* isomer. However, since the *ortho* sulfonate of 1-phenyl-dodecane is inferior to its *para* isomer in detergency ability, it is conceivable that

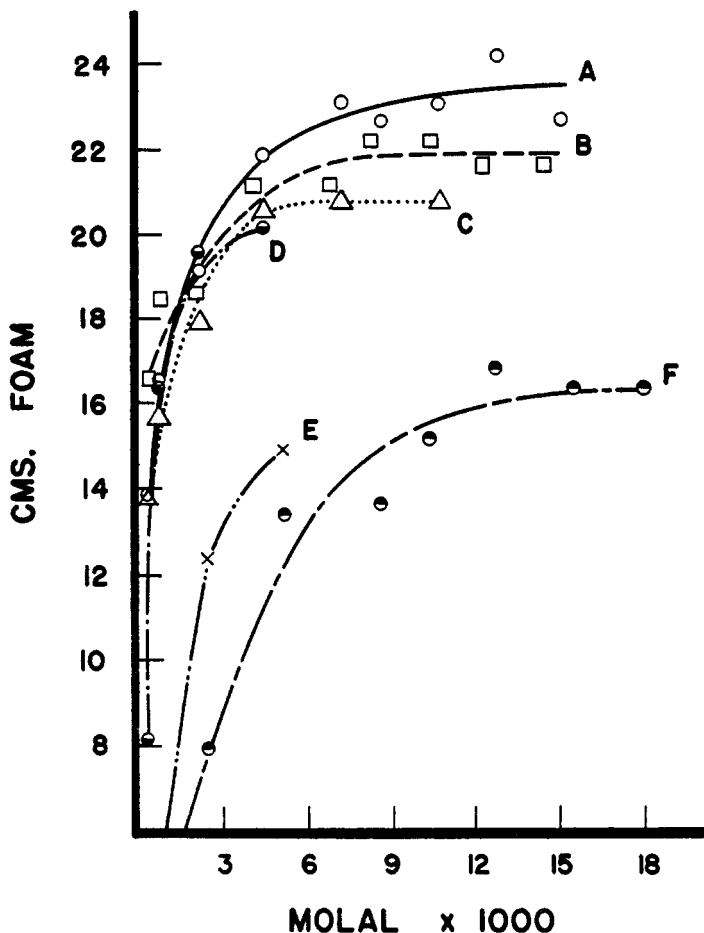


FIG. 4. CENTIMETERS OF FOAM vs. CONCENTRATION FOR AQUEOUS SOLUTIONS OF SODIUM ALKYL BENZENESULFONATES AT 60°.

- | | |
|---|---|
| A. Sodium <i>p</i> -(1-butyloctyl)benzenesulfonate | D. Sodium <i>p</i> -dodecylbenzenesulfonate |
| B. Sodium <i>p</i> -(1-methyldodecyl)benzenesulfonate | E. Sodium <i>o</i> -octylbenzenesulfonate |
| C. Sodium <i>o</i> -dodecylbenzenesulfonate | F. Sodium <i>p</i> -octylbenzenesulfonate |

the low *ortho* content in a crude isomeric sulfonate mixture from a 2-phenylalkane would not have as great an adverse detergency effect as one might expect from the relatively high *ortho* content present in a crude isomeric sulfonate from a 1-phenylalkane. Conversely, sulfonation of a hydrocarbon having the phenyl group in a position remote from the end of an alkyl chain, such as 5-phenyl-dodecane, produces essentially a *para* isomer; but the detergency, due to the configurational change in moving the phenyl group from the 1- to the 5-position, is relatively poor compared either to the *ortho* or *para* isomers obtained by sulfonation of 1-phenyldodecane. Although our data are too limited at present to establish a sound correlation between structure and detergency, it is evident that

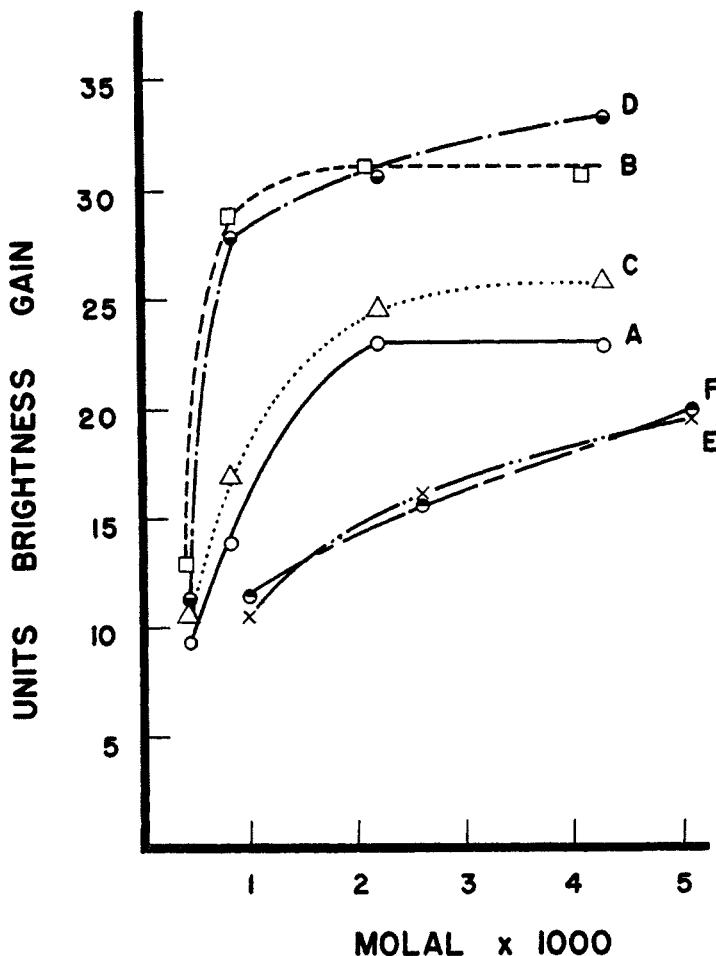


FIG. 5. DETERGENCY—UNITS BRIGHTNESS GAIN *vs.* CONCENTRATION FOR AQUEOUS SOLUTION OF SODIUM ALKYL BENZENESULFONATES AT 60°.

- | | |
|---|---|
| A. Sodium <i>p</i> -(1-butyloctyl)benzenesulfonate | D. Sodium <i>p</i> -dodecylbenzenesulfonate |
| B. Sodium <i>p</i> -(1-methyldodecyl)benzenesulfonate | E. Sodium <i>o</i> -octylbenzenesulfonate |
| C. Sodium <i>o</i> -dodecylbenzenesulfonate | F. Sodium <i>p</i> -octylbenzenesulfonate |

both the position of the sulfonate group and of the phenyl group are factors which with chain length affect the deterative properties of these compounds.

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EXPERIMENTAL¹

Preparation of ketones. The *n*-heptyl phenyl ketone and *n*-undecyl phenyl ketone were prepared by the Friedel-Crafts reaction of octanoyl chloride and lauroyl chloride respectively with benzene (1).

1-Phenyldodecane. In a 1-liter, 3-necked flask equipped with a mechanical stirrer, a water cooled reflux condenser, and a thermometer was placed 60 g. (0.23 mole) of *n*-undecyl phenyl ketone, 40 g. of potassium hydroxide, 300 ml. of triethylene glycol, and 30 ml. of hydrazine hydrate. The stirrer was started and the contents of the flask were heated at 135° for a period of three hours. The condenser was converted for "take-off" and enough water and excess hydrazine were removed to raise the temperature of the reaction mixture to 195°. At this temperature the water condenser was replaced with an air-cooled condenser and the reaction mixture was refluxed at 195° for 6 hours. The reaction mixture was cooled, transferred to a separatory-funnel and the two layers were separated. The upper layer was washed with water and extracted with ethyl ether. The lower layer was diluted with water and also extracted with ether. The combined ether extracts were dried over magnesium sulfate; the drying agent and solvent were removed, and the product was vacuum distilled. The fraction boiling at 148° (1 mm.); n_D^{20} 1.4818, weighed 42.5 g. (75%). This compound has recently become commercially available from the Eastman-Kodak Company.

1-Phenyloctane. The *n*-heptyl-phenyl ketone was reduced in the manner described above for 1-phenyldodecane. The hydrocarbon distilled at 95–97° (0.5 mm.); n_D^{25} 1.4826 in a 70% yield, m.p. –35°. Heilbron (13) reports –7° and Paquette, *et al.* (1) –46° for the melting point. The infrared spectrum was in agreement with that published by the American Petroleum Institute (5).

Sodium octylbenzenesulfonate isomers. In the usual apparatus (500 ml.) was placed 75 g. (0.4 mole) of 1-phenyloctane. At an initial temperature of 15°, 76 g. of 20% oleum was added from the dropping-funnel during the course of about 20 minutes; the temperature of the mixture was not allowed to exceed 30°. After complete addition of oleum, the temperature of the reaction mixture was raised and held at 55° for 1.5 hours. The resultant sulfonic acid mix was added to about 600 ml. of approximately 10% aqueous sodium hydroxide and finally was adjusted to pH 7. The precipitate was collected, washed with about 200 ml. of water, and dried in a vacuum oven at 80°. The product was recrystallized from water to give 80 g. (70%) of sodium *p*-octylbenzenesulfonate.

The aqueous filtrate (approx. 800 ml.) obtained after removal of the *para* isomer was evaporated to dryness and extracted several times with dry ether. The ether-soluble extract (23 g.) consisted of *ortho* isomer contaminated with a small amount of unreacted oil, sulfones, and other unidentified products. The ether-insoluble fraction consisted of inorganic salt with a small amount (3 g.; 2%) of *para* isomer that was recoverable by alcohol extraction. The ether-soluble portion was redissolved in ether and extracted several times in a separatory-funnel with water. The ether layer contained about 1 g. of unreacted or degraded oil, sulfones, and other unidentified matter. The aqueous layer on evaporation to dryness gave 22 g. (19%) of essentially pure sodium *o*-octylbenzenesulfonate that was further purified by recrystallization from the minimum of anhydrous ethanol.

Sodium dodecylbenzenesulfonate isomers. 1-Phenyldodecane (20 g., 0.08 mole) treated

¹ We thank M. Malakoff and T. Delaney for assistance in the synthesis work and the determination of surface tension; R. Diaz and H. Paitchel for the foam, wetting and detergency tests; J. Gillis for the elemental analyses, and W. E. Thompson and K. O. Kellenbach for identifying the sulfonate isomers by interpretation of the infrared spectra.

with 21 g. of 20% oleum under the conditions described for 1-phenyloctane gave 23 g. (81%) of sodium *p*-dodecylbenzenesulfonate. This isomer was isolated as a water-insoluble fraction (solubility about 0.03% at room temperature) by recrystallization from hot water. The water-soluble fraction, with the exception of about 2% of free oil or sulfones, consisted of sodium *o*-dodecylbenzenesulfonate.

1-Phenyldodecane (51 g., 0.21 mole) was sulfonated with 18 g. (0.22 mole) of sulfur trioxide vapor diluted with air according to the technique of Gilbert, *et al.* (14). The products of reaction isolated consisted of 57.0 g. (79%) of *para* isomer, 8.0 g. (11%) of *ortho* isomer, 4.0 g. of sodium sulfate, and 2.5 g. of sulfone and phenylalkane.

In a large scale preparation of about 1.3 kilograms of sodium dodecylbenzenesulfonate, the crystallization of the *para* isomer from ethanol was attempted (10). The product obtained from alcohol was found by infrared analysis to be predominately *para* isomer admixed with *ortho* and *meta* isomers. Recrystallization from water gave uncontaminated *para* isomer and a filtrate containing crude *ortho* and *meta* sulfonates. A small amount (2.5 g.) identified by infrared spectra as sodium *m*-dodecylbenzenesulfonate was isolated by repeated crystallizations of the water-soluble fractions from tetrahydrofuran.

2-Phenyl-2-tridecanol. In the usual apparatus (1 liter) was placed 19.4 g. (0.80 mole) of magnesium and 200 ml. of dry ether. Methyl iodide (113.6 g., 0.80 mole) was added dropwise at a rate to maintain gentle refluxing and the refluxing then was continued for two hours. To the Grignard reagent was added 195.7 g. (0.75 mole) of *n*-undecyl phenyl ketone dissolved in about 150 ml. of warm dry ether and the mixture was refluxed for about two hours. After standing overnight, the contents of the flask was poured into about 125 ml. of concentrated hydrochloric acid and 500 g. of cracked ice, transferred to a separatory-funnel and the two layers separated. The aqueous layer was extracted three times with ether. The ether extracts were all combined and washed successively with water, 5% sodium bicarbonate solution, water, and then dried over magnesium sulfate. The drying reagent and solvent were removed and distillation of the product from a Claisen flask, followed by redistillation through a column (38 x 1.3 cm.) packed with glass helices gave 150 g. (75%) at 128° (0.5 mm.).

Anal. Calc'd for $C_{19}H_{32}O$: C, 82.54; H, 11.67.

Found: C, 82.65; H, 11.53.

2-Phenyl-(1 or 2)-tridecene. The 2-phenyl-2-tridecanol (75 g., 0.27 mole) was treated with 6 g. of anhydrous copper sulfate and 2 g. of potassium hydrogen sulfate and heated at approximately 200° for about 4 hours. The product, distilled from a Claisen flask and then through a glass helices-packed column (38 x 1.3 cm.), weighed 57 g. (82%). The majority distilled at 122° (0.5 mm.) and the infrared spectrum indicated this fraction to be 2-phenyl-1-tridecene.

2-Phenyltridecene. The unsaturated 2-phenyltridecene readily absorbed the theoretical amount of hydrogen when placed in a Parr hydrogenator with ethanol as solvent and 5% palladium-on-charcoal as a catalyst. The hydrogenated product, after removal of solvent and catalyst, was washed four times with 96% sulfuric acid, twice with 5% sodium bicarbonate solution, and finally with water. After drying over magnesium sulfate the hydrocarbon was distilled from 105–109° (0.3 mm.); n_D^{25} 1.4799, in a 75% yield.

Anal. Calc'd for $C_{19}H_{32}$: C, 87.61; H, 12.39.

Found: C, 87.56; H, 12.24.

5-Phenyl-5-dodecanol. This compound was prepared in essentially the same manner as 2-phenyl-2-tridecanol by the reaction of *n*-butylmagnesium bromide with *n*-heptyl phenyl ketone. Distillation of the reaction product gave 99.2 g. (82%) from 130–134° (1.1 mm.). The majority of the product was redistilled through a glass helices-packed column (38 x 1.3 cm.) at 134–135° (1.3 mm.).

Anal. Calc'd for $C_{18}H_{30}O$: C, 82.38; H, 11.52.

Found: C, 82.37; H, 11.25.

5-Phenyl-(4 or 5)-dodecene. To 45 g. (0.19 mole) of 5-phenyl-5-dodecanol was added 5 g. of anhydrous copper sulfate; the mixture was kept at about 200° for a period of 4 hours.

The dehydration was much more vigorous than was experienced in the dehydration of 2-phenyl-2-tridecanol. The product was distilled through a glass helices-packed column (38 x 1.3 cm.); 25.3 g. (61%) collected at 95° (0.2 mm.).

5-Phenyldodecane. 5-Phenyldodecene (25 g.), 0.1 g. of 5% palladium-on-charcoal, and 300 ml. of ethanol were reduced in a Parr hydrogenator at 3 atmospheres pressure. The theoretical amount of hydrogen was absorbed in about one hour. The catalyst and solvent were removed and the hydrogenated material was washed five times with 96% sulfuric acid, twice with 5% sodium bicarbonate solution, and finally with water. Distillation through a glass helices-packed column (38 x 1.3 cm.) gave 16.6 g. (67%) of product at 88–90° (0.2 mm.).

In another experiment 42.7 g. of this compound was prepared in the above described manner. Distillation through a Podbielniak column gave 40 g. at 175° (19 mm.); n_D^{25} 1.4803, d_4^{25} 0.8467.

Anal. Calc'd for $C_{18}H_{30}$: C, 87.45; H, 12.55.

Found: C, 87.39; H, 12.40.

Sodium (1-methyldodecyl)benzenesulfonate isomers. The 2-phenyltridecane (21 g., 0.08 mole) was sulfonated with 22 g. of 20% oleum in the same manner as described for 1-phenyloctane. The light yellow sulfonic acid mix obtained was cooled to 35° and then added to about 200 ml. of approximately 10% sodium hydroxide and the solution was adjusted to pH 7. The white sulfonate slurry was cooled overnight at 5°. The precipitate (I) was filtered and dried in a vacuum oven at 90°; weight 43.0 g. Evaporation of the filtrate to dryness gave an additional 4 g. Several treatments of I with warm dry ether gave an extract consisting of 2.8 g. of a yellowish oily tacky material. Infrared analysis (Fig. 2D) showed this fraction to be mostly *ortho* with some *para* but no *meta* isomer being present. Crystallization with acetone gave an amorphous product that contained a trace of *para* isomer; the S-benzylthiuronium derivative formed was an oil. A 10-g. sample of I was recrystallized from 100 ml. of 10% ethanol to yield: Crop (A), 4.3 g.; Crop (B), 1.0 g. The infrared spectra of these fractions (Fig. 2E) were shown to be free from *ortho* isomer and to be entirely *para* isomer with a slight possibility that a trace of *meta* isomer may be present.

Sodium (1-butyloctyl)benzenesulfonate isomers. 5-Phenyldodecane (35 g., 0.14 mole) was sulfonated with 37 g. of 20% oleum under the same conditions as given above for 2-phenyltridecane. The neutralized slurry was transferred to a separatory-funnel and the lower clear solution was removed. The upper layer consisting of a creamy gel was taken to dryness, digested with warm dry ether, and the insoluble inorganic salt was removed. The ether solution was placed in a separatory-funnel and extracted with water. The layers were separated and evaporated to dryness. The ether layer gave a sticky oil that was identified by its infrared spectrum as unreacted phenylalkane and sulfones. The aqueous layer from the ether extract contained 35 g. of material that was found to be predominantly *para* sulfonate with a negligible amount of *ortho* isomer being present. On recrystallization from acetone, the amorphous product was shown by infrared (Fig. 2F) analysis to be entirely sodium *p*-(1-butyloctyl)benzenesulfonate.

The original aqueous layer (from which the gel had been removed) was taken to dryness, combined with the ether insoluble-portion from the gel, and subjected to an ether digestion and water extraction treatment. In this manner, an additional 4.5 g. of mostly sodium *p*-(1-butyloctyl)benzenesulfonate was isolated from inorganic salt and ether-soluble oil. The inorganic salt was not entirely free of *para* sulfonate but no significant amounts of either *ortho* or *meta* isomer could be detected in the fraction. The yield of isolated sodium *p*-(1-butyloctyl)benzenesulfonate was about 80%.

Surface tension. The surface tension of the solutions at 25° was determined by the du Nouy ring method, employing a calibration curve of the dial reading plotted against the surface tension of pure liquids. The curve for sodium *p*-dodecylbenzenesulfonate was limited by the poor solubility.

Foam height. The foam heights were determined by the Ross-Miles method (15) at 60°.

The curve for sodium *o*-octylbenzenesulfonate could not be completed at the higher concentrations for lack of material.

Wetting. The wetting properties were obtained by recording the time in seconds for a No. 6 Mount Vernon duck canvas disk 1-inch in diameter to sink beneath the surface of liquid at 60°. The solution to be tested (350 ml.) was placed in a 400 ml. beaker, which was immersed in a constant temperature bath, and the disk was dropped in the solution in a horizontal position. Each test was repeated several times, usually five, until consistent values for wetting time were obtained.

Detergency. The detergency values, *i.e.*, per cent brightness gain with a test fabric soiled cloth, were obtained at various concentrations. A maximum probable error of ± 1.9 brightness gain (per cent reflectance) was determined from a total of 20 replicate tests with sodium *p*-dodecylbenzenesulfonate. The procedure used for testing was as follows: The sodium alkylbenzenesulfonates at various concentrations were dissolved in distilled water at 80° and then allowed to cool to 60° for testing in a Terg-O-Tometer. The operation conditions were: Speed, 150 cpm; Time, 20 minutes; Temperature, 60°; Volume, 350 ml.; Soiled cloth, 6 pieces of Test Fabric #26 (16) cut 1.5 x 2 inches. On completion of the washing, the test pieces were mildly rinsed by hand in lukewarm tap water and subsequently ironed dry. The test cloths were then measured for reflectance on a Hunter Color and Color-Difference Meter.

Infrared spectra. The infrared absorption spectra were determined with a Perkin-Elmer, Model 21 Infrared Spectrophotometer. The hydrocarbons (Fig. 1) were determined in the liquid phase using a sodium chloride cell (0.025 mm.) and the sulfonates (Fig. 2) were determined in Nujol mulls.

SUMMARY

The hydrocarbons 1-phenyloctane, 1-phenyldodecane, 2-phenyltridecane, and 5-phenyldodecane have been prepared and sulfonated. The isomers obtained upon sulfonation have been isolated as their sodium salts and identified by derivative formation and infrared spectra. The position of the sulfonate group in the benzene ring as well as the position of the phenyl group and length of the alkyl chain have a pronounced effect upon the surface active properties of sodium alkylbenzenesulfonates. The *ortho* sulfonates have lower surface tension values, are better wetting agents and give higher foam heights than their respective *para* isomers. In detergency, the *para* compounds are superior to their *ortho* isomers. Also, as the phenyl group is moved toward the center of the chain of an alkylbenzene the yield of *ortho* isomer obtained on sulfonation decreases. The *para* isomer formed from a hydrocarbon in which the phenyl group is located about the center of the alkyl chain possess physical and chemical properties that resemble an *ortho* isomer obtained from a compound containing the phenyl group located about the end of the chain.

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