Sodium Alkylbenzenesulfonates from Phenols

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Ten sodium alkylbenzenesulfonates of high purity were prepared. The key step in the synthesis involves the Newman-Kwart rearrangement of O-aryl to S-aryl dimethylthiocarbamate. This step makes possible conversion of a phenol to an organic sulfur compound, which then can be oxidized to an alkylbenzenesulfonic acid.

In studying the effect of surfactant molecular structure on surface activity it is important that the materials be of high purity. Consequently, a method of preparing sodium alkylbenzenesulfonates from phenols has been developed, in which a sulfonate group is substituted for the hydroxyl group. This method of synthesis avoids the formation of isomers. Ten sodium alkylbenzenesulfonates were prepared, using the synthetic scheme described below. These materials were purified by recrystallizing from 85% aqueous ethanol until no further change in the infrared spectrum was detected. *S*-Benzylthiuronium derivatives of the alkylbenzenesulfonates were prepared for identification.

The scheme illustrated in Figure 1 was used for preparing sodium 4-dodecylbenzenesulfonate (I), sodium 2-methyl-4-dodecylbenzenesulfonate (IV), sodium 2,6-dimethyl-4-decylbenzenesulfonate (V), sodium 2,6-dimethyl-4-dodecylbenzenesulfonate (VI), and sodium 2,6-dimethyl-4-hexadecylbenzenesulfonate (VIII). The reactions used are well known and are not described in detail here. Fries rearrangement of the esters to the 4-alkanoylphenols utilized aluminum chloride as catalyst and nitrobenzene as solvent (*5*). The carbonyl groups were reduced by the Huang-Minlon modification of the Wolff-Kishner reduction (*2*). Preparation of *O*- and *S*-aryl dimethylthiocarbamates from phenols has been described by Newman and Karnes (*14*) and Relles and Pizzolato (*15*). For this study the *O*-aryl compounds were held at 300° until thin-layer chromatographic analysis indicated complete reaction. For oxidizing *S*-aryl dimethylthiocarbamates to sulfonic acids, a 10 to 1 molar ratio of 30% hydrogen peroxide was added dropwise at room temperature to a 10% solution of the substrate in formic acid. After an induction period of about 30 minutes, the temperature rose considerably. The mixture was stirred overnight. The oxidation reaction is described in greater detail elsewhere (*7*).

Procedures used in preparing other alkylphenol intermediates differed from that just outlined, but in every case the phenol was converted to the sulfonate by the scheme shown in Figure 1. Thus, sodium 2-dodecylbenzenesulfonate (III) was prepared from 2-dodecylphenol. In preparing the latter compound, the conditions used for the Fries rearrangement of phenyl dodecanoate were modified. To favor 2- and 4-dodecanoylphenol, a high reaction temperature and titanium tetrachloride catalyst were used (*11*). Both 2- and 4-dodecanoylphenol were produced in this reaction. These compounds were easily separated by distillation, however, since 2-isomer has an appreciably lower boiling point because of chelation.

The intermediate 3-dodecylphenol used in preparing sodium 3-dodecylbenzenesulfonate (II) was prepared from 3-methoxybenzaldehyde by the scheme illustrated in Figure 2. Refluxing in a Dean-Stark apparatus with phosphoric acid in xylene dehydrated the alcoholic product of the Grignard reaction (*8*). Reduction of the olefin used the

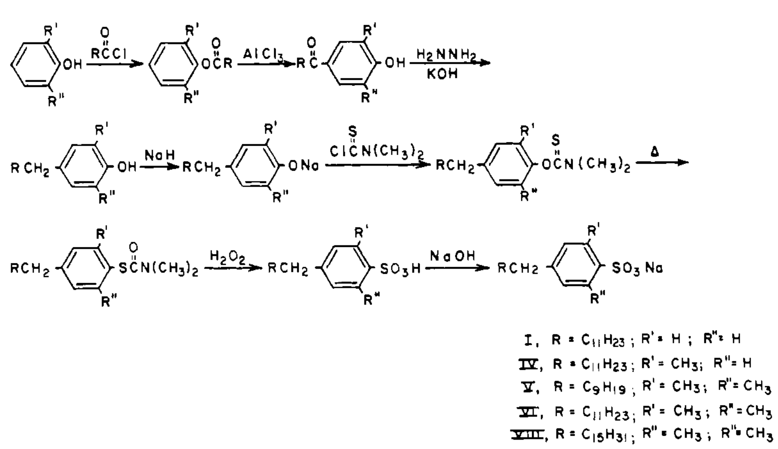
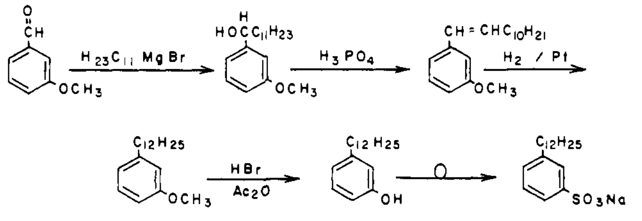
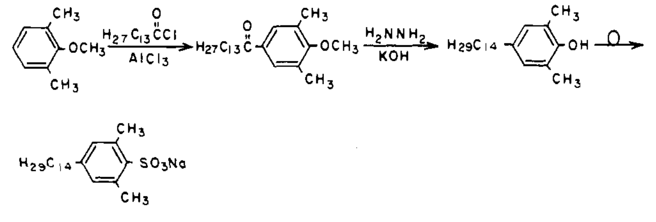


Figure 1. Preparation of sodium 4-alkyl benzenesulfonates



II

Figure 2. Preparation of sodium 3-dodecylbenzenesulfonate



VIII

Figure 3. Preparation of sodium 2,6-dimethyl-4-tetradecylbenzenesulfonate

procedure developed by Brown and Brown (*6*). Hydrolysis of the methyl ether was very difficult with 48% HBr alone; addition of acetic anhydride, however, resulted in complete hydrolysis in 48 hours (*12*).

The two-step process shown in Figure 3 was used for making 2,6-dimethyl-4-tetradecylphenol. This compound served as an intermediate in preparing sodium 2,6-dimethyl-4-tetradecylbenzenesulfonate (VII). The 2,6-dimethyl-4-tetradecanoylanisole was prepared by Friedel-Crafts addition of tetradecanoyl chloride to 2,6-dimethylanisole (*1*). Reduction of carbonyl groups by the Huang-Minlon modification of the Wolff-Kishner reduction has been reported to be accompanied by hydrolysis of all methyl ether groups which may be present (*4*). After 48 hours, about 25% of the methoxyl groups remained, so that extracting with Claisen's alkali was necessary to obtain pure 2,6-dimethyl-4-tetradecylphenol. This procedure is only slightly more efficient for preparing 2,6-dimethyl-4-alkylphenols than that illustrated in Figure 1.

Intermediate phenols used in preparing sodium 4-(1-propylnonyl)benzenesulfonate (IX) and sodium 2-methyl-4-(1-propylnony)benzenesulfonate (X) were synthesized as illustrated in Figure 4. Phenol was used as the starting material in the sequence leading to IX, and *o*-cresol served as starting material for preparing X. The alkanoylphenols were converted to the alkanoylanisoles with dimethyl sulfate (*10*). Procedures for the other steps are given above.

Physical properties of many of the compounds prepared in this work are given in Tables I through IV. Compounds described elsewhere are not included for comparison except for three sodium alkylbenzenesulfonates. The sodium alkylbenzenesulfonates are grouped in Table IV according to structural type. Intermediates are listed in the other tables in corresponding order. Olefinic intermediates are mixtures of isomers; therefore, their properties are not tabulated. Esters and miscellaneous compounds (Table I) and phenols (Table II) are listed without comment because they are higher homologs of familiar materials. Intermediates leading to VIII were not purified sufficiently for accurate analysis.

Properties of the *O*-aryl dimethylthiocarbamates are listed in Table III. Initial crystallization of these compounds was slow, but once seed crystals were available, recrystallization was not difficult. Elemental analyses of *O*-3-dodecylphenyl, *O*-4-(1-propylnonyl)phenyl, and *O*-2-methyl-4-(1-propylnonyl)phenyl dimethylthiocarbamate are not listed because these compounds did not crystallize. Since

Table I. Esters and Miscellaneous Compounds[a]

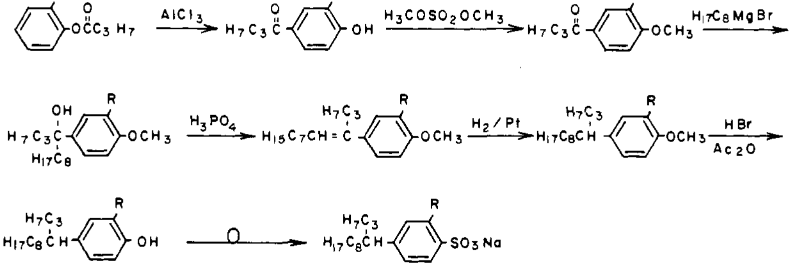
Compound	M.P., °C, or B.P., °C/Mm	n_D^{20}	d_4^{20}
Phenyl dodecanoate	134-8/0.02	1.4865	
2-Methylphenyl dodecanoate	162-4/0.2	1.4828	0.9317
2,6-Dimethylphenyl decanoate	158-9/1.0	1.4836	0.9371
2,6-Dimethylphenyl dodecanoate	170-3/0.5	1.4825	0.9307
Phenyl butanoate	70-3/0.05	1.4948	1.0200
2-Methylphenyl butanoate	66-70/0.05	1.4942	1.0042
1-(3-Methoxyphenyl)-1-dodecanol	184-7/0.5	1.4921	0.8894
1-(3-Methoxyphenyl)-2-dodecene	146-8/0.05	1.5008	0.8895
3-Dodecylanisole	32-33		
3,5-Dimethyl-4-methoxytetradecanophenone	40-41		
4-Methoxybutyrophenone	123-5/0.4	1.5385	1.0451
4-(1-Propylnonyl)anisole	132-4/0.03	1.4880	0.8934
3-Methyl-4-methoxybutyrophenone	105-7/0.08	1.5392	1.0361
2-Methyl-4-(1-propylnonyl)anisole	145-50/0.04	1.4946	0.8988

[a] Experimental values for carbon and hydrogen content of all compounds were within 0.4% of theoretical.

Table II. Phenols[a]

Phenol	M.P., °C, or B.P., °C/Mm
2-Dodecanoylphenol	45-46.5
2-Methyl-4-dodecanoylphenol	66-67
2,6-Dimethyl-4-decanoylphenol	48-49.5
3-Dodecylphenol	32-33
2-Dodecylphenol	43-44
2-Methyl-4-dodecylphenol	40-41
2,6-Dimethyl-4-decylphenol	59.5-61.0
2,6-Dimethyl-4-tetradecylphenol	69-70
4-(1-Propylnonyl)phenol	140-43/0.05
2-Methyl-4-(1-propylnonyl)phenol	144-50/0.02

[a] Experimental values for carbon and hydrogen content of all compounds were within 0.4% of theoretical.



IX, R = H
X, R = CH_3

Figure 4. Preparation of sodium 4-(1-propylnonyl)benzenesulfonates

Table III. Dimethylthiocarbamates[a]

Aryl Group	*O*-Aryl Dimethylthiocarbamates, M.P., °C	*S*-Aryl Dimethylthiocarbamates, M.P., °C, or B.P., °C/Mm
4-Dodecylphenyl	46-47	43-44
3-Dodecylphenyl		181-3/0.02
2-Dodecylphenyl	35-36	181-3/0.02
2-Methyl-4-dodecylphenyl	41-42	213/0.07
2,6-Dimethyl-4-decylphenyl	30-31	35-36
2,6-Dimethyl-4-dodecylphenyl	52.5-54	48-49
2,6-Dimethyl-4-tetradecylphenyl	55-55.5	54-54.5
4-(1-Propylnonyl)phenyl		162-6/0.15
2-Methyl-4-(1-Propylnonyl)-phenyl		180-3/0.05

[a] Experimental values for nitrogen and sulfur content of all compounds were within 0.4% of theoretical.

Table IV. Sodium Alkylbenzenesulfonates[a]

	Alkylbenzene	*S*-Benzylthiuronium Derivative, M.P., °C
I	4-Dodecylbenzene	117-18[b]
II	3-Dodecylbenzene	94.5-95.5[c]
III	2-Dodecylbenzene	105-06[d]
IV	2-Methyl-4-dodecylbenzene	100-01
V	2,6-Dimethyl-4-decylbenzene	80-81
VI	2,6-Dimethyl-4-dodecylbenzene	93-94
VII	2,6-Dimethyl-4-tetradecylbenzene	96-97
VIII	2,6-Dimethyl-4-hexadecylbenzene	100-01
IX	4-(1-Propylnonyl)benzene	117-18
X	2-Methyl-4-(1-propylnonyl)benzene	127-28

[a] Experimental values for sulfur and sodium content of all sodium alkylbenzenesulfonates were within 0.3% of theoretical except for sodium content of compound X, for which difference was 0.44%. Experimental values for nitrogen and sulfur content of all *S*-benzylthiuronium salts were within 0.4% of theoretical. [b] Reported m.p. 117-18° (*9, 16*). [c] Reported m.p. 92-94° (*9*) and 97-98° (*16*). [d] Reported m.p. 101-03° (*9*) and 100-01° (*16*).

distilling leads to rearrangement, these compounds were not purified for analysis. Although these compounds were dark in color, infrared and NMR spectra were consistent with those expected. Properties of the *S*-aryl dimethylthiocarbamates are also given in Table III. Purification of these compounds was possible in every case, by either recrystallizing or distilling.

Properties of the sodium alkylbenzenesulfonates and *S*-benzylthiuronium derivatives are listed in Table IV. Melting points of derivatives and infrared spectra of I, II, and III are in satisfactory agreement with those reported in the literature (*9*). That the melting points of the derivatives of I and IX are identical is fortuitous. Asinger and coworkers showed that as the point of substitution of the *p*-phenylsulfonate group on an alkyl chain is varied from the end of the chain toward the middle, there result first a drop and then a rise in the melting point of the *S*-benzylthiuronium derivative (*3*). Gray and coworkers found the melting point of the derivative of 4-(1-butyloctyl)benzenesulfonate to be higher than that of 1-dodecylbenzenesulfonate (*9*).

Melting points were taken using a capillary melting point apparatus and are corrected. Elemental analyses were by Galbraith Laboratories, Knoxville, Tenn. 37921; all analyses were within 0.4% of theoretical. Infrared spectra were taken using a Perkin-Elmer Model 421 grating spectrophotometer. Spectra of sodium sulfonates were measured on mineral oil mulls; spectra of other compounds were measured on solutions in carbon disulfide or carbon tetrachloride. Densities were determined using a pycnometer, and refractive indices were found with an Abbe refractometer.

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