Synthesis and Biodegradability of Isomeric Sodium p-(Thia-n-dodecyl)-benzenesulfonates

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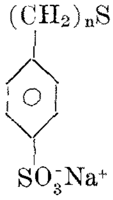
Abstract

In an attempt to prepare improved biodegradable detergents, the eleven possible isomers of sodium p-(thia-*n*-dodecyl)benzenesulfonate have been synthesized. Preliminary biodegradability tests of these compounds show that the biodegradability of sodium p-1-thia-*n*-dodecylbenzenesulfonate is greater than that of LAS.

Introduction

THE SEARCH FOR IMPROVED biodegradable detergents has shown that, of the various isomers of sodium dodecylbenzenesulfonate, p-(*n*-dodecyl)benzenesulfonate is the most rapidly biodegraded (6). It is still unknown, however, to what degree the straight-chain alkylbenzenesulfonates (LAS) can solve the problem of water pollution (7). It was therefore of interest to determine if the skeleton of the LAS could be made more susceptible to biological attack by introducing hetero atoms like sulfur into the alkyl side chain. This investigation was undertaken to attempt to synthesize the thia derivatives of sodium p-(*n*-dodecyl)benzenesulfonate in which the different methylene groups are successively replaced by sulfur. None of the eleven possible isomers of sodium p-(thia-*n*-dodecyl) benzenesulfonate, the synthesis of which is here described, has been reported in the literature.



$n + m = 10$

Experimental

Material

Apparatus. The nuclear magnetic resonance spectra were recorded on a Varian 60 Mc spectrometer at 60C. The samples were dissolved in deuterated water with sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as internal standard ($\tau = 10.00$ for the trimethylsilyl protons). The infrared spectra were recorded on a Beckman IR 9 spectrophotometer using KBr-pellets. Temperature measurements are uncorrected.

Sodium p-(1-Thia-n-dodecyl)benzenesulfonate. Sodium (11.5 g, 0.50 mole) was dissolved in 250 ml of absolute ethanol and 55 g of thiophenol (0.50 mole) was added. Under external cooling, 95 g of *n*-undecyl chloride (0.50 mole) was added and then the reaction mixture was boiled under reflux for 3.5 hr. The precipitated sodium chloride was filtered, the solvent evaporated, and the residue dissolved in a mixture of petroleum ether and benzene, from which the phenyl *n*-undecyl sulfide crystallized on cooling. Yield 102 g (0.39 mole, 77%); mp 31–33C (lit. (4) mp 33.8C).

A solution of 20 g (0.08 mole) of phenyl *n*-undecyl sulfide in 10 ml of chloroform was dropped during 1 hr into 30 ml (0.45 mole) of chlorosulfonic acid with stirring at 25C. The reaction mixture was then poured on ice and the organic material extracted with ether. The ether solution was washed with water, sodium bicarbonate solution, again with water, and dried. Evaporation of the solvent yielded 18 g (0.05 mole, 65%) of crude p-(1-thia-*n*-dodecyl)benzenesulfonyl chloride. Its infrared spectrum showed the typical absorption bands for the sulfonyl chloride group at 1175 and 1370 cm^{-1}. In 150 ml of 60% ethanol, 4.0 g (0.10 mole) of sodium hydroxide and 18 g (0.05 mole) of the sulfonyl chloride were dissolved, and the mixture was stirred for several hours at room temperature. On cooling the solution in an ice-bath, sodium p-(1-thia-*n*-dodecyl)benzenesulfonate crystallized in colorless leaflets. After three recrystallizations from 50% ethanol, 12 g (0.03 mole, 65%) was obtained.

Anal. Calc. for $C_{17}H_{27}O_3S_2Na$ (366.53); C, 55.71; H, 7.43; S, 17.50. Found: C, 55.91; H, 7.46; S, 17.61.

Sodium p-(2-Thia-n-dodecyl)benzenesulfonate. The procedure for preparing sodium α-chloro-p-toluenesulfonate (2) was adapted to a bench-scale method. Sodium p-toluenesulfonate (68 g, 0.35 mole) was placed in a 500-ml four-necked flask provided with a mechanical stirrer, a thermometer and a gas-inlet and -outlet. The flask was immersed in an oil-bath at 120C, and, with stirring of the dry salt, chlorine was passed in. The internal temperature rose to 145C. After 75 min the reactant had gained 11 g. The crude reaction product was twice recrystallized from 90% ethanol. The analysis as well as the nuclear magnetic resonance (NMR) spectrum indicated that this product was a mixture of mono-and dichlorinated toluenesulfonate. Its NMR spectrum in deuterated water (TMS as an external standard) showed, beside the signals for the phenyl protons around τ 2.4 and the singlet for the benzyl protons at τ 5.37, another singlet at τ 3.04 due to the benzal proton. From the intensities of these signals the proportion of the compounds was calculated to be about 60% α-monochloro- and 40% α-dichlorotoluenesulfonate.

To a solution of 26 g of this mixture (about 0.10 mole) and 6.0 g (0.15 mole) of sodium hydroxide, 400 ml of 40% ethanol and 26 g (0.15 mole) of *n*-decanethiol were added, and the reaction mixture was boiled under reflux for 2 hr. After neutralization with hydrochloric acid, the solution was cooled, and the precipitated colorless leaflets of sodium p-(2-thia-*n*-dodecyl)-benzenesulfonate were recrystallized three times from 50% ethanol. Yield 18 g (0.05 mole, approximately 50%).

Anal. Calc. for $C_{17}H_{27}O_3S_2Na$ (366.53); C, 55.71; H, 7.43; S, 17.50. Found: C, 55.76; H, 7.47; S, 17.38.

General Procedure for the Synthesis of Sodium p-(N-Thia-n-dodecyl)-benzenesulfonates for $N = 3$ to 11 inclusive. (See Table I for results.) The chloroalkylbenzene (1.0 mole) was added dropwise during

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[1] Pioneering Research Division Post-doctoral Research Fellow, 1963–1964.

TABLE I

Yields and Analyses of Sodium p-(Thia-*n*-dodecyl)benzene Sulfonates

Chloroalkylbenzene	Sodium p-(Chloroalkyl)-benzenesulfonate	Yield %	Sodium p-(Thia-*n*-dodecyl)-benzenesulfonate	Yield %	Carbon, % (Calc.—55.71) Found	Hydrogen, % (Calc.—7.43) Found	Sulfur, % (Calc.—17.50) Found
(2-Chloroethyl)-benzene[a]	Sodium p-(2-chloroethyl)-benzenesulfonate	82	Sodium p-(3-thia-*n*-dodecyl)-benzenesulfonate	65	55.48	7.45	17.43
(3-Chloropropyl)-benzene[a]	Sodium p-(3-chloropropyl)-benzenesulfonate	93	Sodium p-(4-thia-*n*-dodecyl)-benzenesulfonate	46	55.83	7.29	17.55
(4-Chlorobutyl)-benzene[b]	Sodium p-(4-chlorobutyl)-benzenesulfonate	55	Sodium p-(5-thia-*n*-dodecyl)-benzenesulfonate	29	55.72	7.48	17.59
(5-Chloropentyl)-benzene[c]	Sodium p-(5-chloropentyl)-benzenesulfonate	32	Sodium p-(6-thia-*n*-dodecyl)-benzenesulfonate	31	55.64	7.33	17.23
(6-Chlorohexyl)-benzene[d]	Sodium p-(6-chlorohexyl)-benzenesulfonate	30	Sodium p-(7-thia-*n*-dodecyl)-benzenesulfonate	34	55.62	7.27	17.69
(7-Chloroheptyl)-benzene[c]	Sodium p-(7-chloroheptyl)-benzenesulfonate	40	Sodium p-(8-thia-*n*-dodecyl)-benzenesulfonate	31	55.89	7.28	17.63
(8-Chlorooctyl)-benzene[c]	Sodium p-(8-chlorooctyl)-benzenesulfonate	40	Sodium p-(9-thia-*n*-dodecyl)-benzenesulfonate	20	55.71	7.22	17.34
(9-Chlorononyl)-benzene[e]	Sodium p-(9-chlorononyl)-benzenesulfonate	20	Sodium p-(10-thia-*n*-dodecyl)-benzenesulfonate	31	55.73	7.48	17.48
(10-Chlorodecyl)-benzene[c]	Sodium p-(10-chlorodecyl)-benzenesulfonate	13	Sodium p-(11-thia-*n*-dodceyl)-benzenesulfonate	32	55.89	7.35	17.29

[a] Eastman Kodak Company, Rochester, New York.

[b] Prepared by the reaction of 3-phenylpropylmagnesium chloride with formaldehyde and chlorination of the resulting alcohol with thionyl chloride.

[c] Sapon Laboratories, Oceanside, New York.

[d] Conant, J. B., and W. R. Kirner, J. Am. Chem. Soc. *46*, 232 (1924).

[e] 9-Phenylnonanol was prepared by an extension of the method of Conant and Kirner[d] from 6-phenylhexylmagnesium chloride and 3-chloropropoxy (9-chlorononyl) benzene (bp 137–140C at 0.5 mm).

1.5 hr to chlorosulfonic acid (10.0 moles) with efficient stirring, and external cooling by a water-bath at temperatures between 0 and 25C. The reaction mixture was stirred for another hour and then poured onto ice. The aqueous mixture was extracted with ether, the ether layer was separated from the water layer, and the ether removed by evaporation in vacuum. The residue was purified by distillation under reduced pressure.

In the case of p-(2-chloroethyl)benzenesulfonyl chloride, the aqueous insoluble product was crystalline. It was purified by two recrystallizations from a mixture of petroleum ether and ether (3:1). Yield 27 g (0.11 mole, 57%); mp 53.5–55C.

Anal. Calc. for $C_8H_8Cl_2O_2S$ (239.13); C, 40.18; H, 3.37; Cl, 29.65; S, 13.41. Found: C, 40.32; H, 3.50; Cl, 29.58; S, 13.30.

The infrared spectrum of this product (potassium bromide) exhibits strong bands at 1180 and 1380 cm^{-1} due to the sulfonyl chloride group and weak bands at 1800 and 1925 cm^{-1} that indicate a 1,4-disubstituted benzene.

The purified chloroalkylbenzenesulfonyl chloride (1.0 mole) was added to a solution of sodium hydroxide (2.0 moles) in water (5.9 ml of water per gram of sodium hydroxide), and the heterogeneous reaction mixture was stirred vigorously until it became homogeneous. The solution was neutralized with hydrochloric acid and evaporated to dryness. Recrystallization of the residue from ethanol yielded crystalline sodium p-(chloroalkyl)benzenesulfonate.

A mixture of equimolecular quantities of sodium p-(chloroalkyl)-benzenesulfonate, sodium hydroxide and n-alkylmercaptan was boiled under reflux for 3 hr. On cooling the solution, the desired product crystallized. Recrystallization from water, or aqueous ethanol, afforded pure crystalline sodium p-(N-thia-*n*-dodecyl)-benzenesulfonate.

Discussion

The structure of these compounds was established by elemental analysis, NMR and infrared spectra. The τ values, intensities and assignments of the NMR signals of the various compounds are given in Table II.

A general feature of all spectra of Table II is an A_2B_2 pattern for the phenyl protons which gives two doublets of equal intensity with $J_{AB} = 8$ cps. This pattern is characteristic of substituents in a benzene ring in the para positions. In most of the spectra the peaks for the benzyl protons and the protons of the methylene groups that are adjacent to the sulfur atom are not separated but rather consist of a multiplet. The observed intensities are in all cases identical with the calculated values.

The infrared spectra show strong absorption bands at 1050 and 1190 cm^{-1} due to the sulfonate group. The region between 2000 cm^{-1} and 1667 cm^{-1} was expanded. The spectra in this range show only two bands around 1810 and 1925 cm^{-1}. This pattern is further evidence for a 1,4-disubstituted benzene (5).

The synthesis of compounds with an isolated sulfur atom in the side-chain was undertaken since the configuration of such an atom is closely analogous to that of a methylene group and would therefore confer on the molecule physical properties similar to those of the LAS compounds. The sodium p-(thia-*n*-dodecyl)-benzenesulfonates were expected to be more biodegradable than LAS since the carbon-sulfur bond is known to be more easily broken than a carbon-carbon bond (3). Also, sulfur compounds are known to frequently undergo enzymic reactions (1).

TABLE II

NMR Spectra of Sodium p-(Thia-*n*-dodecyl)benzenesulfonates

Compound	Aromatic H		—CH_2S— and $PhCH_2$—	—CH_2—	—CH_3	Intensities
1-thia-	2.40	2.86	7.20	8.73	9.20	2:2:2:18:3
2-thia-	2.30	2.75	7.60 6.40	8.68	9.08	2:2:2:2:16:3
3-thia-	2.30	2.86	7.30	8.65	9.05	2:2:6:14:3
4-thia-	2.29	2.86	7.50	8.66	9.05	2:2:6:14:3
5-thia-	2.25	2.83	7.50	8.60	9.00	2:2:6:14:3
6-thia-	2.27	2.84	7.50	8.54	9.02	2:2:6:14:3
7-thia-	2.26	2.84	7.50	8.53	9.00	2:2:6:14:3
8-thia-	2.25	2.85	7.50	8.62	9.03	2:2:6:14:3
9-thia-	2.23	2.85	7.50	8.63	8.98	2:2:6:14:3
10-thia-	2.33	2.90	7.50	8.71	8.90	2:2:6:14:3
11-thia-	2.34	2.92	7.50	8.65	7.96	2:2:4:16:3

TABLE III

Biodegradability of Sodium p-(N-thia-*n*-dodecyl)benzenesulfonate

Sodium p-(N-thia-*n*-dodecyl)-benzenesulfonate	Number of days for 100% biodegradation	
	Method	
N	A[a]	B[b]
0 [c]	8	7
1	5	5
2	9	7
3	15	14
4	14	14
5	>15	>14
6	>15	>14
7	>15	>14
8	>15	>14
9	>15	>14
10	>15	>14
11	>15	>14

[a] Shake fiask mehod. Allred, R. C., E. A. Setzkorn and R. L. Huddleston, JAOCS *41*, 13 (1964).

[b] River die-away method, Setzkorn, E. A., R. L. Huddleston and R. C. Allred, *Ibid*, *41*, 826 (1964).

[c] LAS.

The results of the preliminary biodegradability tests are shown in Table III.

Since the introduction of a single heteroatom in the alkyl side-chain of the LAS molecule has bestowed increased biodegradability on the molecule in one case, possibilities would appear to exist for the synthesis of new and improved biodegradable detergents.

The biological and technical behavior of the isomeric sodium p-(thia-*n*-dodecyl)benzenesulfonates are being further investigated, and the results will be reported in detail in another paper.

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Analysis of Surfactants Using Pyrolysis-Gas Chromatography[1]

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Abstract

A pyrolysis-gas chromatographic method has been devised for the rapid analysis of surfactants and surfactant mixtures. The method involves pyrolysis of the surfactant in a unit directly attached to a gas chromatograph. The resulting pyrolysis products give characteristic gas chromatographic patterns which are useful for analysis of the original surfactant.

This method is useful for the qualitative identification of surfactants either alone, in synthetic mixtures, or in commercial products. In many cases, the technique can also be used for semiquantitative estimation of (1) relative amounts of the individual components in mixtures and (2) structural distribution of the surfactants. The method is amenable to both solid and liquid and both light-duty and heavy-duty detergent formulations.

Introduction

THE RAPID, INEXPENSIVE analysis of surfactants is of considerable interest to the detergent industry. Such analytical techniques as ultraviolet and infrared spectrometry and nuclear magnetic resonance are of particular value in the case of individual surfactants, but these techniques can give only limited information about surfactant mixtures found in many commercial detergent products.

Pyrolysis-gas chromatography (P-GC) as an analytical tool for surfactants is not reported in the literature, although the technique has been developing rapidly as a simple and useful tool for identification of nonvolatile organic compounds (1–4), polymers (5–7), and volatile compounds (8,9). The present paper discusses the application of P-GC to surfactants. For surfactants, it is a relatively simple method which can give a surprising amount of information, both qualitative and semiquantitative. The experimental technique involves pyrolysis of the surfactant in the absence of air at 650C in a unit which is directly attached to the inlet port of a gas chromatograph. The pyrolysis products are immediately swept into the gas chromatograph by the carrier gas, helium. Under these conditions, most common surfactant materials decompose into characteristic products from which the original surfactants can be identified by interpretation of the resulting gas chromatogram.

The data are useful for qualitative identification of surfactants in mixtures and in commercial detergent products. In many cases, semiquantitative estimation of the various components in the surfactant mixtures is also possible. In addition, pertinent surfactant structural information, such as the molecular weight distribution of the hydrophobic portion of the molecule, can often be estimated.

Usefulness of this analytical method is shown by data on several individual surfactants and some synthetic surfactant mixtures and commercial detergent products.

Experimental

Apparatus

The pyrolysis unit is a modification of one previously described (10) and is shown in Figure 1. Also required are an external magnet of sufficient strength to move the soft iron bar, a cylindrical stainless steel pyrolysis cup (¼ in. O.D. by ½ in. height), and a cup remover as shown in Figure 1. The tapered end of the cup remover is just small enough so that its machined end can be forced into the top of the pyrolysis cup. On the cup remover's

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[1] Presented at the AOCS meeting, Houston, 1965.

[2] Company name formerly "California Research Corporation."