Sodium *p*-[1-(*n*-Nonylthio) Ethyl] Benzene Sulfonate: A New, Third Generation, Biodegradable Surfactant

M. A. LINTER and L. LONG, JR., U.S. Army Natick Laboratories, Natick, Massachusetts 01760

Abstract

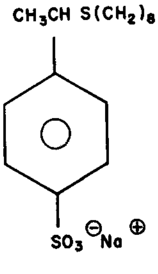
Synthesis of sodium *p*-[1-(*n*-nonylthio)ethyl] benzene sulfonate has been achieved by two distinct routes, starting with ethylbenzene, in overall yields of 26% and 27%. Preliminary tests indicate a somewhat increased detergency to that of LAS, and superior biodegradability to LAS.

Introduction

Although great progress has been made in combating the problem of foam caused by undegraded synthetic detergents in rivers and sewage plants, it has not yet been finally solved. Only 33% of the people in the United States have facilities for completely treating sewage, another 23% have facilities for limited sewage treatment and 8% have no treatment facilities at all. The remaining 36% depend upon septic tanks and cesspools in which the synthetic detergents are not sufficiently degraded (1). Furthermore, undegraded linear alkylbenzene sulfonates, LAS, have been reported to be several times more toxic to fish than undegraded alkylbenzene sulfonates, ABS (2).

As a result of the foregoing considerations, a third generation of surfactants may be required.

In a previous communication (3), we reported the synthesis of the 11 isomers of sodium *p*-(thia-*n*-dodecyl)benzenesulfonate thereby providing an insight into the biodegradability behavior of linear alkylbenzene sulfonates in which one methylene group has been replaced with a sulfur atom. As sodium *p*-(*n*-dodecyl)benzene sulfonate is the most rapidly biodegraded of the various isomers of sodium dodecyl benzene sulfonate (4), the 12 atom side chain, utilized in the first study reported by us (3), was retained. However, it has been found that increased solubility results from branching in the side chain to form the 2-phenyl substituted dodecyl moiety (Swisher, personal communication) and for our continuation of the initial investigation, we decided to prepare sodium *p*-[1-(*n*-nonylthio)ethyl]benzene sulfonate [I].



I

Experimental Procedures

The nuclear magnetic resonance spectra were recorded on a Varian 60 MHz spectrometer at 60 C. External TMS was provided as a reference for those spectra determined in deuterated water and internal TMS for those in other solvents (δ = 0.00 for methylsilyl protons). The infrared spectra were recorded on a Perkin-Elmer 137 Infracord. Temperature measurements, boiling and melting points are uncorrected.

p-Ethylbenzenesulfonyl chloride was prepared in 74% yield by the method of Moralli (5), bp (1.1 mm) 117–119 C, N_D^{30} 1.5429; bp (14–16 mm) 166–170 C (5); bp (14 mm) 143 C, N_D^{20} 1.5469 (Swisher, personal communication).

p-(1-Bromoethyl)Benzene Sulfonyl Chloride. To a refluxing solution of 102.25 g (0.5 mole) of *p*-ethylbenzene sulfonyl chloride in 400 ml of carbon tetrachloride was added, dropwise, a solution of 80 g (0.5 mole) of bromine in 400 ml of carbon tetrachloride. The reaction mixture was stirred at reflux for a total of 4 hr, the solvent removed and product distilled, bp (1.75 mm) 161–163 C, yield 124.67 g (88.7%), N_D^{23} 1.5821. The product solidified upon standing, mp 38–40 C. The infrared spectrum (neat film) showed absorptions at 3100 cm^{-1} (aromatic C–H stretching), 2995 and 2945 cm^{-1} (aliphatic C–H stretching), 1380 and 1180 cm^{-1} (due to $-SO_2Cl$)[6] and 841 cm^{-1} (para substitution). The NMR spectrum (neat) showed signals due to four aromatic protons at 7.72–8.17 δ (quartet, J = 8 cps, the A_2B_2 system characteristic of para substitution in a phenyl ring), one benzal proton at 5.28–5.40 δ (quartet, J = 7 cps) and three methyl protons at 2.00–2.10 δ (doublet, J = 7 cps).

Analysis. Calculated for $C_8H_8BrClO_2S$ (283.5); C, 33.86; H, 2.82; Br, 28.22; Cl, 12.52; S, 11.29. Found: C, 33.83; H, 3.08; Br, 28.37; Cl, 12.48; S, 11.06.

p-(1-Bromoethyl)Benzene Sulfonamide. Dry ammonia was passed into a stirred solution of 20 g (70.6 mmoles) of *p*-(1-bromoethyl)benzene sulfonyl chloride in 250 ml of acetone for 1 hr. The mixture was filtered to afford 3.56 g of white solid (NH_4Cl) and a yellow solution. Removal of the solvent gave a yellow oil. Addition of 50 ml of 5% aqueous hydrochloric acid gave a pale yellow solid which was collected by filtration and recrystallized twice from benzene to afford 14.25 g (76.6%) of *p*-(1-bromoethyl) benzene sulfonamide, mp 126.5–127.8 C. The infrared spectrum (KBr pellet) showed absorptions at 3380 and 3300 cm^{-1} (NH_2–N–H stretching), 1335 and 1185 cm^{-1} ($-SO_2NH_2$)[7] and 840 cm^{-1} (para substitution). The NMR spectrum (acetone, d_6) showed signals due to four aromatic protons at 7.62–8.03 δ (quartet, J = 8 cps, A_2B_2 system), two protons of the amide NH_2 as a broad peak centered at 6.54 δ, one benzal proton at 5.27–5.62 δ (quartet, J = 6.5 cps) and three methyl protons at 1.96–2.07 δ (quartet, J = 6.5 cps).

Analysis. Calculated for $C_8H_{10}BrNO_2S$(264): C, 36.36; H, 3.79; Br, 30.30; N, 5.30; S, 12.12. Found: C, 36.52, 36.51; H, 3.79, 3.64; Br, 30.00, 30.23; N, 5.28, 5.24; S, 12.38, 12.41.

p-[1-(n-Nonylthio)Ethyl]Benzene Sulfonamide. To a stirred solution of 3.46 g (21.55 mmoles) of *n*-nonyl mercaptan and 862 mg (21.55 mmoles) of sodium hydroxide in 50 ml of absolute ethanol, heated to effect solution and formation of the mercaptide salt, was added, dropwise, a solution of 5.0 g (21.55 mmoles) of *p*-(1-bromoethyl)benzene sulfonamide in

150 ml of absolute ethanol. A cloudiness developed and, after the addition was complete, the reaction mixture was refluxed for 2 hr. The resulting clear solution was evaporated to give a yellow oily solid which was extracted with ether and filtered. The solid which remained was washed with water until washings showed a negative silver nitrate test and the remaining solid, 1.12 g, set aside. The ether was evaporated from the filtrate to give 5.83 g of pale yellow solid. The infrared spectra of the two solids were identical, total yield 6.95 g (93.9%). The combined product was recrystallized twice from benzene to afford a white solid, mp 74–75 C. The infrared spectrum ($CHCl_3$) showed absorptions at 3420 and 3300 cm^{-1} (NH_2–N–H stretching), 2940 and 2875 cm^{-1} (aliphatic C–H stretching), 1160 and 1340 cm^{-1} ($-SO_2NH_2$)[7] and 840 cm^{-1} (para substitution). The NMR spectrum ($CDCl_3$) showed signals due to four aromatic protons in an A_2B_2 system at 7.37–8.07 δ (quartet, J = 8 cps), two protons of the amide NH_2 as a broad peak centered at 5.50 δ, one benzal proton at 3.80–4.23 δ (quartet, J = 7 cps), two methylene protons, assigned to the methylene group adjacent to the sulfur atom, at 2.17–2.50 δ (triplet, J = 7 cps) and twenty protons, assigned to the remainder of the nonyl group and the methyl attached to the benzal carbon, as a complex multiplet from 0.68–1.82 δ.

Analysis. Calculated for $C_{17}H_{29}NO_2S_2$(343.6): C, 59.43; H, 8.51; N, 4.08; S, 18.67. Found: C, 59.42, 59.55; H, 8.63, 8.71; N, 4.10, 4.11; S, 18.69, 18.70.

Ethyl p-(1-Bromoethyl)Benzene Sulfonate. To a stirred solution of 28.35 g (0.1 mole) of *p*-(1-bromoethyl)benzenesulfonyl chloride in 100 ml of absolute ethanol, maintained at a temperature below 20 C, was added, dropwise, a solution of 0.1 mole of sodium ethoxide [from 2.3 g (0.1 g atom) of sodium] in 100 ml of absolute ethanol. The solution turned milk white and the temperature was maintained near 20 C throughout the addition. The addition required 10 min and was allowed to stir for an additional 45 min, at which time a test for the presence of base, using phenophthalein as indicator, was negative. The reaction mixture was poured into 400 ml of water, extracted with 200 ml of chloroform and then with two 100 ml portions of chloroform. The combined organic extracts were washed with 50 ml of water, 150 ml of aqueous sodium bicarbonate, two 60 ml portions of water, dried over sodium sulfate, filtered and solvent removed to give 29.01 g (99.9% yield) of colorless liquid which decomposed when an attempt was made to distil it at 1.0 mm. The infrared spectrum (neat) showed absorptions at 2980 and 2910 cm^{-1} (aliphatic C–H stretching), 1180 and 1360 cm^{-1} ($-SO_2-OR$)[7] and 844 cm^{-1} (para substitution). The NMR spectrum (neat) showed signals due to four aromatic protons in an A_2B_2 pattern at 7.52–7.92 δ (quartet, J = 8 cps), one benzal proton at 5.00–5.35 δ (quartet, J = 7 cps), two methylene protons of the ethyl group at 3.82–4.17 δ (quartet, J = 7 cps), three protons of the methyl group attached to the benzal carbon at 1.78–1.90 δ (doublet, J = 7 cps) and three methyl protons of the ethyl group at 0.95–1.18 δ (triplet, J = 7 cps). The product was used without further purification.

Sodium p-[1-(n-Nonylthio)Ethyl]Benzene Sulfonate. To a stirred solution of 21.3 g (0.1331 mole) of *n*-nonyl mercaptan and 10.648 g (0.2662 mole) of sodium hydroxide in 50 ml of absolute ethanol at 5 C (previously heated to 90 C to effect solution and formation of the mercaptide) was added, dropwise, 39 g (0.1331 mole) of ethyl *p*-(1-bromoethyl)benzene sulfonate. A white precipitate formed and the temperature was maintained below 8 C throughout the addition. The mixture was slowly allowed to warm to room temperature and filtered to give a white solid. Evaporation of the filtrate gave a pale yellow solid which was extracted with ether to remove any unreacted starting material. Infrared spectra of the original solid collected from the precipitate and the residue after the ether extraction were practically identical. The combined product was recrystallized twice from 95% ethanol to give 18.91 g of sodium *p*-[1-(*n*-nonylthio)ethyl]benzene sulfonate (38.8%). The infrared spectrum of the product exhibited absorptions at 2900 and 2980 cm^{-1} (aliphatic C–H stretching), 1380 and 1470 cm^{-1} (C–H deformation), 1059 and 1140 cm^{-1} ($-SO_3^-Na^+$)[7], 640 cm^{-1} (sulfur attached to a primary carbon) and 615 cm^{-1} (sulfur attached to a secondary carbon). The NMR spectrum (deuterated water with external TMS) showed signals due to four aromatic protons, in an A_2B_2 pattern at 7.07–7.78 δ (quartet, J = 8 cps), 1 benzal proton at 3.78–4.21 δ (quartet, J = 7 cps), 2 methylene protons, assigned to the methylene group adjacent to the sulfur atom, at 2.18–2.51 δ (triplet, J = 7 cps) and 20 protons, assigned to the remainder of the nonyl group and the methyl attached to the benzal carbon, as a complex multiplet from 0.65–1.83 δ.

Analysis. Calculated for $C_{17}H_{27}NaO_3S_2$(366): C, 55.71; H, 7.43; S, 17.50. Found: C, 55.44, 55.59; H, 7.27, 7.54; S, 17.69, 17.78.

Hydrolysis of p-[1-(n-Nonylthio)Ethyl]Benzene Sulfonamide. A mixture of 2 g (5.82 mmoles) of *p*-[1-(*n*-nonylthio)ethyl]benzene sulfonamide and 15 ml of 80% sulfuric acid (prepared by carefully mixing three parts of concentrated sulfuric acid and one part of water) was stirred at 165 C for 30 min. The mixture was poured into 100 ml of water and made basic by the addition of 4N sodium hydroxide solution. The resulting solution was evaporated to leave a dark solid which was placed on a Soxhlet extraction apparatus and extracted with ethanol. The ethanol was removed from the extraction solution to give a tan solid which was taken up in water and dilute hydrochloric acid added to a pH of ca. 8. The water was removed to give a pale tan solid which was crystallized from benzene to give 1.24 g (57.7%) of a colorless solid whose infrared spectrum was identical with that of authentic sodium *p*-[1-(*n*-nonylthio)ethyl]benzene sulfonate.

Sodium p-[1-(n-Nonylsulfinyl)Ethyl]Benzene Sulfonate. To a stirred solution of 587 mg (2.74 mmoles) of sodium metaperiodate in 50 ml of water at 4 C was slowly added a solution of 1.0 g (2.74 mmoles) of sodium *p*-[1-(*n*-nonylthio)ethyl]benzene sulfonate in 50 ml of water. The mixture was allowed to warm to room temperature and stirred for 24 hr. The mixture was concentrated and methanol added. Filtration gave a white solid (sodium iodate) and a yellow solution. Removal of solvent from the filtrate gave a yellow oily solid which was crystallized from ethanol to afford 590 mg (56.7%) of sodium *p*-[1-(*n*-nonylsulfinyl)ethyl]benzene sulfonate as white plates. The infrared spectrum (KBr pellet) showed absorptions at 2890 and 2960 cm^{-1} (aliphatic C–H stretching), 1055 and 1135 cm^{-1} ($-SO_3^-Na^+$)[7], 1015 cm^{-1} (S = O of sulfoxide)[7], 840 cm^{-1} (para substitution) and 685 cm^{-1} (sulfur attached to aromatic carbon). The NMR spectrum (deuterated water with external TMS) showed signals due to four aromatic protons in an A_2B_2 pattern at 7.32–8.03 δ (quartet, J = 8 cps), one benzal proton at 3.40–3.83 δ (quartet, J = 7 cps) and 22 protons assigned to the nonyl group and the methyl group attached to the benzal carbon as a complex broad multiplet from 0.73–1.73 δ. The signals due to the methyl of the nonyl group are found occurring as a triplet (J = 7 cps) at 0.81–1.07 δ and the other methyl group as a doublet (J = 7 cps) at 1.35–1.47 δ.

Analysis. Calculated for $C_{17}H_{27}NaO_4S_2$: C, 53.38; H, 7.12; S, 16.76. Found: C, 53.55, 53.40; H, 7.33, 7.37; S, 16.55, 16.82.

Aqueous Ammonolysis of p-(1-Bromoethyl)Benzene Sulfonyl Chloride to p-(1-Hydroxyethyl)Benzene Sulfonamide. To 1.70 g (6 mmoles) of *p*-(1-bromoethyl) benzenesulfonyl chloride at 40 C was added, in portions, 25 ml of concentrated aqueous ammonium hydroxide. The resulting yellow solid was washed with water and crystallized from ethanol to give 1.15 g (95.8%) of white solid, mp 118.5–119.5 C. The infrared spectrum (KBr pellet) showed absorptions at 3400 and 3300 cm^{-1} (NH_2–N–H stretching), 1160 and 1315 cm^{-1} ($-SO_2NH_2$)[7], 1100 cm^{-1} (C–O stretching of a secondary alcohol) and 840 cm^{-1} (para substitution). The NMR spectrum (acetone, d_6) showed signals due to four aromatic protons, in an A_2B_2 pattern, at 7.45–8.05 δ (quartet, J = 8 cps), a broad peak centered at 6.52 δ due to the two NH_2 protons of the amide, one benzal proton as a quartet (J = 7 cps) at 4.75–5.10 δ, one proton assigned to the hydroxyl group as a singlet at 4.39 δ and a three proton doublet (J = 7 cps) at 1.35–1.47 δ due to the methyl group. The spectral data combined with the elemental analysis identified the product as *p*-(1-hydroxyethyl)benzene sulfonamide.

Analysis. Calculated for $C_8H_{11}NO_3S(201)$: C, 47.76; H, 5.47; N, 6.97; S, 15.92. Found: C, 47.28, 47.17; H, 5.57, 5.45; N, 7.15, 6.94. S, 16.03, 15.86.

Discussion

The purified sodium *p*-[1-(*n*-nonylthio)ethyl]benzene sulfonate was submitted for testing to determine biodegradability, solubility, surface tension, wetting and detergency. The results are shown in Table I. The introduction of the heteroatom in the alkyl side chain combined with the branching of the chain has produced a molecule with increased biodegradability compared to a standard sample of LAS and increased detergency compared to a commercial product in which linear alkylbenezene sulfonates have been compounded with other ingredients.

TABLE I

Biodegradability, Solubility, Surface Tension, Wetting and Detergency Tests

Properties	Sodium *p*-[1-(*n*-nonylthio) ethyl] benzene sulfonate	Sodium *p*-(*n*-dodecyl)[a] benzene sulfonate	Ultrawet[b] K-soft
Biodegradability[c]	2 days/100%	3 days/100%	
Solubility (g/100 cc H_2O), 25 C	ca 2		>33
Surface tension (25 C, dyne cm^{-1})			
0.01% in Dist. H_2O	59.2		51.2
0.05% in Dist. H_2O	48.6		39.1
Draves Wetting Test at 25 C (sinking seconds)			
0.1% in H_2O	16		8
Detergency tests at 60 C in H_2O			
Soil removal	36.4%		34.0%
Whiteness retention	88.7%		87.1%

[a] Standard sample of linear alkylbenzene sulfonates (LAS) supplied by the Soap and Detergent Association.
[b] Linear alkylbenzene sulfonate (90% active).
[c] Shake flask method (8).

Although the test results are of a preliminary nature, they indicate that it may be possible to synthesize a compound containing a heteroatom in the side chain of a linear alkylbenzene sulfonate which will have greater biodegradability and detergency than the commercial products currently in use.

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