Synthesis and Rigorous Purification of Sodium Alkylbenzene Sulfonates

R.S. Budhram and **E.J. Eisenbraun***
Department of Chemistry, Oklahoma State University, Stillwater, OK 74078

The detergent properties of sodium alkylbenzene sulfonates frequently do not allow the use of conventional solvents and methods of organic chemistry for isolation and purification. The preparation of large quantities of highly purified linear and branched alkylbenzene sulfonates was achieved through purification of the corresponding methyl sulfonate ester obtained in one step by chlorosulfonation of the hydrocarbon and quenching the reaction mixture with methanol. Preparative HPLC of the methyl sulfonate ester and the use of special techniques in analytical HPLC provided highly purified sodium alkylbenzene sulfonates.

Linear and branched alkylbenzene sulfonates are of considerable interest to the petroleum industry because of their surfactant properties in tertiary oil recovery. The surfactant activity varies, depending on chain length, chain branching and position of the benzene ring on the alkyl chain (1). In thermodynamic studies of sodium sulfonates related to tertiary oil recovery, it is crucial that highly purified material be used to place the thermodynamic data on a credible basis.

Rigorous purification of sodium alkylbenzene sulfonates is a formidable task. Because of their detergent properties, these compounds generally do not lend themselves to the use of conventional organic solvents for isolation and purification.

The synthesis of alkylbenzene sulfonates also presents problems, particularly in the generation of unwanted isomers during sulfonation of the benzene ring. Isolation of crystalline sodium sulfonate from this mixture was difficult because of detergent action (3,4). Separation and purification to a single isomer could not be achieved.

EXPERIMENTAL PROCEDURES

Synthesis of alkylbenzenes. 4-Phenyloctane, 3a. A 12-l flask equipped with an overhead mechanical stirrer, a metal, multi-tube condenser and a thermocouple probe was flushed with nitrogen and charged with two l of 2 M butylmagnesium chloride (4 mol) in ether. The reagent was diluted with two l of anhydrous ether, and the reaction flask was cooled in an ice-water bath and 600 g (4 mol) of n-butyrophenone, **1a**, in one l of anhydrous ether were added drop by drop over one hr. After addition, the mixture was heated at reflux for two hr, cooled and quenched with 100 ml of dilute HCl. It was then poured into dilute HCl and ice, and the layers were separated. The aqueous layer was extracted with ether and the combined extracts were washed with dilute HCl and water and dried ($MgSO_4$), filtered, and concentrated to 844 g of crude alcohol, **2a**. A small quantity (10 g) was Kugelrohr distilled to give a colorless lqiuid, bp 180 C (0.3 mm Hg). Gas chromatography and nuclear magnetic resonance studies indicated the mixture to be alcohol **2a**, alkene **1b**, and unreacted ketone **1a**, in the approximate ratio 8:1:1.

*To whom correspondence should be addressed.

The crude alcohol, **2a** (Grignard product) was stirred overnight with an excess of acidified 2,4-DNP reagent and filtered to remove **1a**. The filtrate was concentrated under reduced pressure and steam distilled from oxalic acid. The distillate was collected in a separatory funnel containing ether. The layers were separated and the aqueous layer was extracted with ether. The combined ether extracts were dried ($MgSO_4$) and concentrated to give 662 g (97% overall yield) of alkene, **2b**.

Trial attempts at hydrogenation of alkene **2b** with 10% Pd/C in acetic acid were unsuccessful. Hydrogen uptake was very slow; after 6 hr, as shown by GC analysis, only partial hydrogenation had occurred. Hydrogenation was achieved in two batches each of 331 g with one l of acetic acid, one ml of conc HCl and 15 g of 10% Pd/C. Under these conditions, hydrogen uptake was very rapid and ceased within one hr. Work-up gave 4-phenyloctane, **3a**, showing a single impurity of shorter retention time in GC analysis.

Purification of **3a** was achieved by fractional distillation through a 2 ft Vigreaux column. The best cuts were redistilled slowly on a spinning band column to achieve approximately 99% purity as shown by capillary GC and HPLC studies. ^{1}H-NMR ($CDCl_3$) δ 7.6-7.3 (m, 5H), 2.75 (m, 1H), 2.0-1.0 (m, 16H); ^{13}C-NMR ($CDCl_3$) ppm 146.2, 128.1 (2c), 127.5 (2c), 125.7, 45.9, 39.5, 36.9, 29.9, 22.9, 20.8, 14.1, 14.0.

Synthesis of alkylbenzenes. 1-Phenyloctane (3b). A 12-l flask, fitted with an overhead mechanical stirrer, a condenser and a sodium carbonate HCl trap, was flushed with nitrogen and charged with 500 g (3.0 mol) octanoyl chloride, one l of benzene, and one l of methylene chloride. To the cooled, stirred mixture, under nitrogen, was added 400 g (3.0 mol) of anhydrous aluminum chloride over a period of 1.5 hr. After stirring for an additional 3 hr at room temperature, the mixture was poured onto crushed ice, filtered through Dicalite and the layers separated. The aqueous layer was washed with ether and the combined organic extract was washed with sodium carbonate, water, dried ($MgSO_4$), filtered and concentrated under reduced pressure to give 498 g (80%) of colorless ketone **1b**, bp 105 C (0.1 mm Hg), lit. (6) bp 166-168 C (14 mm Hg). Ketone **1b** was purified further by the preparation and repeated recrystallization of the semicarbazone, mp 125-126 C, and regeneration to **1b** with conc HCl and ether extraction.

Catalytic hydrogenation of 320 g (1.57 mol) of ketone **1b** with Pd/C at 40 psi and room temperature for 1 hr gave 290 g (97%) of 1-phenyloctane **3b**. This was purified by fractional distillation using a spinning band column, bp 70-72 C (0.1 mm); lit. (1) 95-97 C (0.5 mm).

Chlorosulfonation of octylbenzenes. 4-n-Octylbenzenesulfonyl chloride (4b). Chlorosulfonic acid (20 g 0.315 mol) was placed in a 250-ml, 3-neck flask equipped with magnetic stirrer, thermometer, addition funnel and nitrogen atmosphere. The flask was immersed in a water bath and 1-phenyloctane (36.7 g; 0.315 mol) was added drop by drop; the temperature was kept between 20 and 25 C.

Evolved HCl was trapped with saturated sodium carbonate solution. After addition was complete, the mixture was stirred for one hr at room temperature. Acid chloride **4b** was isolated by extraction with CCl_4 to give 21.8 g (90%).

Chlorosulfonation of octylbenzenes. Methyl 4-(4-octyl) benzenesulfonate, 5a. 4-Phenyloctane, **3a**, (247 g, 1.3 mol) was added drop by drop to stirred chlorosulfonic acid (233 g, 2.0 mol) in an ice-water bath at 20–25 C. Evolved HCl was trapped with saturated sodium carbonate solution. After addition was complete, the mixture was stirred for one hr at room temperature, cooled with an ice-water bath and quenched by dropwise addition of methanol until reaction ceased. The solution was diluted with ether, washed with water, dried ($MgSO_4$), and concentrated to give 250 g (80%) of methyl ester, **5a**, as a yellow oil.

Ester **5a** was passed through neutral alumina using n-hexane and then treated with activated charcoal. Further purification using a silica column in the Waters Prep LC 500 System and eluting with n-hexane gave 200 g (65%) of purified methyl sulfonate **5a**. ^{1}H-NMR ($CDCl_3$) δ 8.1–7.3 (m, 4H), 3.69 (s, 3H), 1.8–0.7 (m, 17H); ^{13}C-NMR ($CDCl_3$) ppm 128.1 (2c), 127.7, 127.6 (2c), 127.1, 55.7, 45.5, 39.8, 36.3, 29.4, 22.5, 20.2, 13.5, 13.4.

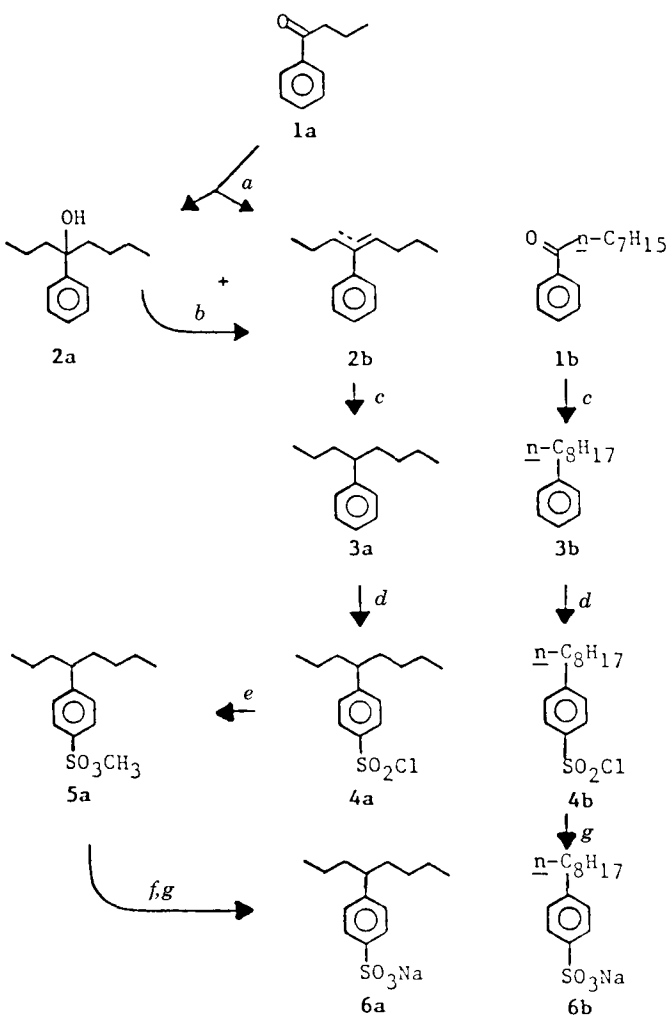
Chlorosulfonation of octylbenzenes. Sodium 4-(4-octyl)-benzenesulfonate, 6a. The methyl sulfonate **5a** (10 g; 0.035 mol) was mixed with a 10% solution of NaOH (2 g; 0.05 mol). The mixture was slowly warmed in a round bottom flask attached to an expansion chamber surmounted by a water condenser. The expansion chamber is essential to control foaming. Heating was discontinued at first signs of foaming. After the vigorous reaction and foaming into the expansion vessel subsided, the reaction mixture was allowed to cool to room temperature. The aqueous layer was poured off from the gel which separated. This gel was washed with water by stirring and decanting, drying to a white solid in a stream of dry nitrogen at room temperature. It was suspended in ether, heated to boiling for a few minutes, cooled to room temperature and filtered. This leaching operation was repeated twice or until all the impurity, which appeared as a shoulder in the LC, had been removed. The white, crystalline solid, shown to be **6a**, was then dried under vacuum overnight. The recovery of **6a** was about 90%. The white, colorless sodium sulfonate **6a** was also recrystallized from isohexane/ethyl acetate, 8:2. The HPLC of the final sample showed only a single peak. ^{1}H-NMR (D_2O) δ 7.8 (d, 2H), 7.25 (d, 2H), 2.5 (m, 1H), 1.65–0.7 (m, 16H); ^{13}C-NMR (D_2O) ppm 151.9, 143.5, 130.3 (2c), 128.4 (2c), 47.9, 41.2, 38.8, 32.2, 25.2, 23.0, 16.5, 16.3.

Chlorosulfonation of octylbenzenes. Sodium n-octyl-benzenesulfonate, 6b. Acid chloride **4b** was poured into a cold solution of 10% sodium hydroxide (0.32 mol). This solution was heated to near boiling to achieve complete hydrolysis of acid chloride **4b**. After cooling, the pH was adjusted to 7 and the sodium sulfonate, **6b**, was filtered, washed thoroughly with cold water and dried under vacuum. 1H-NMR (DMSO-d_6) δ 7.48 (d, 2H), 7.15 (d, 2H), 2.5 (m, 3H), 1.5 (m, 2H), 1.25 (m, 9H), 0.86 (m, 3H); ^{13}C-NMR δ (D_2O) ppm 148.5, 143.2, 131.1 (2c), 128.3 (2c), 38.1, 34.5, 33.7, 32.1 (2c), 32.0, 25.3, 16.5.

RESULTS AND DISCUSSION

The hydrocarbons **3a** and **3b**, as shown in Scheme 1, were prepared in overall yields of 85% and 86% from n-butyrophenone and benzene, respectively. Sulfonation of **3a** and **3b** with neat chlorosulfonic acid at room temperature readily gave the acid chlorides **4a** and **4b**. *n*-Octylbenzenesulfonyl chloride, **4b**, was isolated in 90% yield by extraction with carbon tetrachloride and distillation. Isolation of the acid chlorides **4a** and **4b** is unnecessary and was found to be experimentally difficult due to formation of emulsions and hydrolysis during extraction with carbon tetrachloride. In addition, hydrolysis to the sulfonic acid lowers the isolated yield, particularly for the branched chain isomer **4a**.

Chlorosulfonation of **3b** gave mainly the para isomer. The ortho and/or meta isomer(s) appear to be present only as an impurity (ca. 1–2% as shown by HPLC) and were not isolated. The low solubility of **6b** in water at room temperature affords a means of separation from inorganic salt, isomeric impurity and other contaminants. It became preferable to neutralize **4b** with sodium hydroxide to **6b** and to purify by repeated crystallization from 95% ethanol. This procedure gave a purified sample (99.8%) of **6b**. Although the straight chain para isomers such as **6b** are crystalline, non-tacky products with low solubil-



SCHEME 1

[a]*n*-C_4H_9MgCl/ether; [b]Oxalic acid, steam; [c]H_2, Pd/C, acetic acid, HCl; [d]$ClSO_3H$; [e]CH_3OH; [f]HPLC on **5a**; [g]NaOH, H_2O, Δ.

ity in water or organic solvents, the ortho and/or meta isomers are sticky, less crystalline compounds that are very soluble in polar or non-polar solvents.

In contrast, this approach failed for the preparation of pure branched chain isomer **6a**. The acid chloride **4a** could be isolated in low yield (49%) only with considerable effort because of the severe emulsion formation mentioned above. To overcome this we quenched the chlorosulfonation product with methanol which directly provided the methyl sulfonate **5a** in high yield (80–90%).

An important advantage in preparing methyl ester **5a** is that purification could be effected at this stage in our attempt to prepare highly purified sodium sulfonate **6a**. Decomposition at the high boiling point (205 C, 0.05 mm Hg) of **5a** prevented distillation. After treating the crude product with decolorizing charcoal and passing through a column of silica, neutral alumina and Dicalite, most of the impurities were removed. Further purification with preparative HPLC using a silica column and *n*-hexane in the Waters Prep LC 500 System gave a sample of the methyl sulfonate **5a** showing approximately 99% purity. A leading shoulder peak could not be removed completely on the basis of a 75% recovery.

Hydrolysis of **5a** with an equimolar amount of sodium hydroxide begins at 80 C and is rapidly exothermic to 100 C, with considerable volume expansion by foaming. This was controlled with an expansion chamber mounted above the reaction flask. Attempts to remove water and methanol by distillation resulted in coloration and decreased yields due to formation of an ether soluble impurity. The sodium sulfonate **6a** was isolated by pouring the hot reaction mixture into 10% aqueous sodium hydroxide, cooling, and gravity filtering the resulting semi-solid gel. The residue was then washed with ice-cold water and air dried.

The purity of the sodium sulfonates, **6a** and **6b**, was established by reverse phase HPLC using a C-18 column and buffered aqueous methanol mobile phase. Water used in preparation of the mobile phase was buffered with 0.005M tetrabutylammonium phosphate (Waters Associates PIC Reagent A). A typical HPLC of crude **6a**, using this analytical method, is shown in Figure 1. Washing the filtered product **6a** with water effectively removes impurity peaks a, b, and c which may be inorganic salts or other polar contaminants. If still present, these may be removed completely by further salting out from cold aqueous solutions or by leaching the barium sulfonate.

An analytical HPLC trace, at this point of purification, revealed impurities d, e and f but not a, b and c. These three impurities, d, e and f, appear to be more soluble in non-polar organic solvents than the sodium sulfonate **6a**. Leaching with ether effectively removed them. They also were removed by crystallizing from ethyl acetate and isooctane (1:5).

Unlike **6b**, crystallization of the branched chain isomer **6a** from organic solvents is difficult. With toluene, solution occurs on heating, but a gel is obtained on cooling. A semi-solid gel is obtained by salting out from water at room temperature. Gel formation was observed by previous workers (1) who concluded that 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. With water, methanol, ethyl acetate, methyl acetate, chloroform, dichloromethane, and nitroethane, the sodium sulfonate is too soluble and does not crystallize. Sodium sulfonate **6a** is not sufficiently soluble in n-hexane, isohexane, isooctane or THF for practical recrystallization.

Prior to treatment with ether or any organic solvent, the sodium sulfonate must be thoroughly dried. Presence of water results in emulsion formation and precipitation of a gel on cooling. Crystallization occurs only on cooling a solution of the dried powdered material. Drying was achieved under a stream of dry nitrogen. Evacuation results in foaming even with traces of water present. Storing over calcium chloride is slow and ineffective. Azeotropic distillation of benzene and water is a possibility but has not been tried because of concern about prolonged heating.

Once all traces of water have been removed from a sample of the sodium sulfonate, the material may be treated as an organic compound, i.e. a solution in ether or methanol may be concentrated under vacuum without foaming.

After leaching with ether, the white crystalline material was filtered using aspirator vacuum and then evacuated overnight in a dessicator using an oil pump.

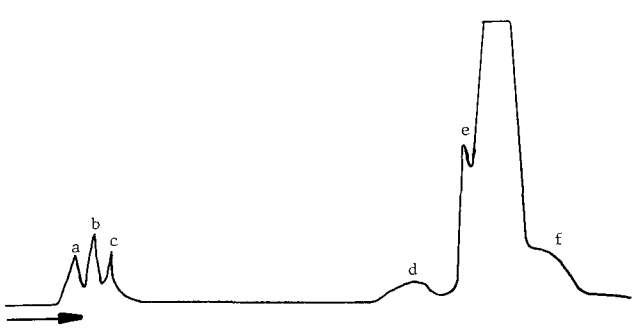


FIG. 1. HPLC trace for crude sodium sulfonate 6a. C18 column, 40% water with PIC A, 60% methanol.

ACKNOWLEDGMENTS

The National Institute for Petroleum and Energy Research, Bartlesville, Oklahoma, and the U.S. Department of Energy supported this work through contract number DE-AS19-83BC10792.

REFERENCES

1. Gray, F.W., J.F. Gerecht and I.J. Krems, *J. Org. Chem. 20:*511 (1955).
2. Gray, F.W., and I.J. Krems, *Ibid. 26:*209 (1961).
3. Doe, P.H., M. El-Emary, W.H. Wade and R.S. Schechter, *J. Amer. Oil Chem. Soc. 55:*505 (1978).
4. Matheson, K.L., and T.P. Matson, *Ibid. 60:*1673 (1983).
5. Doe, P.H., M. El-Emary, W.H. Wade and R.S. Schechter, *Ibid. 55:*513 (1978).
6. Neckers, D.C., *J. Org. Chem. 36:*1838 (1971).

[Received December 13, 1985]