[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Sulfination of Aryllithium Compounds. The Preparation of Sodium *o*-, *m*- and *p*-*n*-Dodecylbenzenesulfonates[1]

BY WILLIAM E. TRUCE AND JOSEPH F. LYONS[2]

During the course of preparing some high molecular weight sodium alkylbenzenesulfonates, the conversion of aryl halides to salts of the corresponding arylsulfonic acids was investigated. Sulfinic acids have been prepared by the reaction of Grignard reagents with sulfur dioxide[3,4]; these are readily oxidized to sulfonic acids.[5,6] In view of the versatility and greater reactivity of organolithium compounds, the preparation of salts of sulfonic acids *via* the corresponding organolithium intermediates was studied.

p-Tolyllithium was sulfinated at 0° with dry sulfur dioxide. The reaction mixture was hydrolyzed and *p*-toluenesulfinic acid was isolated in 68% yield based on *p*-bromotoluene. It was subsequently converted to the corresponding barium sulfonate using hydrogen peroxide, in an over-all yield of 60% based on the aryl bromide. Similarly, *m*-bromotoluene and *o*-bromotoluene were converted to the corresponding sulfonates (see Table I).

TABLE 1

ISOMERIC BARIUM TOLUENESULFONATES AND THEIR S-BENZYLTHIURONIUM SALTS

Isomer	Yield, %[a]	S-Benzylthiuronium salts M. p., °C.	Nitrogen, % Found	Nitrogen, % Calcd.
Para	60[b]	182[c]		
Meta	33[b,d]	155–156[e]	8.30	8.28
Ortho	31[d]	179.5-180.5[e,f]	8.33[f]	8.28

[a] Yield of pure product based on the aryl bromide. [b] Monohydrated salt. [c] Melting point 182° reported by Chambers and Watt, *J. Org. Chem.*, **6**, 376(1941); present derivative did not depress the melting point of an authentic sample of S-benzylthiuronium *p*-toluenesulfonate. [d] Low yields for ortho and meta isomers believed to be due to instability of intermediate sulfinic acids; see Troeger and Voigtlander–Tetzner, *J. prakt. Chem.*, **54**, 513(1896), and Tröger and Hille, *ibid.*, **71**, 201 (1905). [e] Did not depress the melting point of the authentic salt prepared by derivatizing the oxidation product of the appropriate thiocresol. [f] After drying at 77°, 2 mm.

To compare this procedure with that employing the Grignard reagent, *p*-tolylmagnesium bromide was likewise sulfinated. Although the sulfination appeared to proceed satisfactorily, hydrolysis of the reaction mixture required prolonged treatment with dilute acid. The yield of *p*-toluenesulfinic acid was low (20%) and a substantial quantity of di-*p*-tolyl sulfoxide[7] (contaminated with some *p*,*p*'-ditolyl) was isolated. This may have been formed through the course suggested by Burton and Davy.[8]

p-Chlorotoluene was also converted to the barium salt of *p*-toluenesulfonic acid *via* *p*-tolyllithium, thus accomplishing a conversion which is not feasible through the Grignard reagent.

In order to test this method on higher homologs, *p*-bromolaurophenone (II) was prepared from *p*-bromobenzoyl chloride and di-*n*-hendecylcadmium.[9] This ketone was reduced to *p*-bromo-*n*-dodecylbenzene (I) using a variation of the Wolff–Kishner method.[10] Although this aryl bromide reacted sluggishly or not at all with magnesium, it reacted readily with lithium and the resulting product was readily sulfinated. Following the same technique used on the lower homologs, with the exception that sodium permanganate was used as the oxidizing agent, sodium *p*-*n*-dodecylbenzenesulfonate (IV) was prepared in 45% yield based on the aryl bromide. *m*-Bromo-*n*-dodecylbenzene and *o*-bromo-*n*-dodecylbenzene were prepared analogously and converted to the corresponding sodium sulfonates (see Table II).

As an alternate method of synthesizing sodium *p*-*n*-dodecylbenzenesulfonate, *p*-bromolaurophenone was treated with aqueous sodium sulfite at elevated temperature and pressure to give sodium *p*-lauroylbenzenesulfonate in 29% yield. The latter compound was then reduced by the Clemmensen method to give sodium *p*-*n*-dodecylbenzenesulfonate in fair yield.

Experimental

A. Synthesis of Isomeric Barium Toluenesulfonates.—The isomeric *o*-, *m*- and *p*-tolyllithium intermediates were prepared in practically quantitative yields in the usual manner[11] from 34.2 g. (0.20 mole) of the appropriate bromotoluene and 3.4 g. (0.48 g. atom) of lithium metal. A total of 150 ml. of ether was present after the addition of the aryl bromide. Dry sulfur dioxide was passed through the cooled reaction mixture (0°) for one hour with stirring. Hydrolysis was effected by pouring the mixture into ice and dilute aqueous base. The alkaline layer was separated, just acidified with hydrochloride acid, and ether extracted. Evaporation of the ether under nitrogen yielded the free sulfinic acid.

This acid was treated with a slight excess of barium hydroxide solution and the mixture was stirred vigorously while an excess of 15% hydrogen peroxide was added in small increments. After boiling the solution to remove unused peroxide, carbon dioxide was introduced to precipitate the excess barium ion as the carbonate. The insoluble material was filtered and the filtrate was evaporated to deposit the barium salt of the toluenesulfonic acid. Data on yields and derivatives prepared are shown in Table I.

Sulfination of *p*-Tolylmagnesium Bromide.—*p*-Tolylmagnesium bromide was prepared in 92% yield in the usual manner from 4.9 g. (0.20 mole) of magnesium and 34.2 g. (0.20 mole) of *p*-bromotoluene. Sulfination was carried out as described in the foregoing experiments. A dense yellowish-white solid separated out during the process. The reaction mixture was poured into dilute acid and ice, but much of the solid remained unaffected. The acidic mixture was heated and ether extracted. The ether layer was extracted with dilute base and this ether layer (I) was reserved. The alkaline layer was acidified and the sulfinic acid was extracted with ether. Evaporation of the ether

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[1] Based on a thesis submitted by Joseph F. Lyons in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Purdue University, June, 1950.

[2] The Texas Company, Beacon, New York.

[3] Rosenheim and Singer, *Ber.*, **37**, 2152 (1904).

[4] Marvel and Johnson, *J. Org. Chem.*, **13**, 822 (1948)

[5] Hann, THIS JOURNAL, **57**, 2166 (1935).

[6] Doering and Beringer, *ibid.*, **71**, 2221 (1949).

[7] Parker, *Ber.*, **23**, 1844 (1890); Hampson, Farmer and Sutton, *Proc. Roy. Soc.* (*London*), **A143**, 151 (1933).

[8] Burton and Davy, *J. Chem. Soc.*, 528 (1948).

[9] Cason, THIS JOURNAL, **68**, 2078 (1946).

[10] Huang-Minlon, *ibid.*, **68**, 2487 (1946).

[11] Gilman, Zoellner and Selby, *ibid.*, **55**, 1252 (1933).

TABLE II

ISOMERIC SODIUM *n*-DODECYLBENZENESULFONATES AND DERIVATIVES PREPARED

Isomer	Yield, %[a]	Sodium, % Found	Sodium, % Calcd.	S-Benzylthiuronium salt M. p., °C.	S-Benzylthiuronium salt Nitrogen, % Found	S-Benzylthiuronium salt Nitrogen, % Calcd.	*p*-Toluidine salt M. p., °C.	*p*-Toluidine salt Nitrogen, % Found	*p*-Toluidine salt Nitrogen, % Calcd.
Para	45	6.56	6.60	117–118[b]	5.68	5.69	138–139.5[c]	3.26	3.23
Meta	35	6.62	6.60	97–98[c]	5.66	5.69	103–104[c]	3.31	3.23
Ortho	16[d]			100–101[c,e]	5.69	5.69			

[a] Over-all yield based on the aryl bromide. [b] Before vacuum drying this derivative melted at 95–97°; after drying at 77° (2 mm.) it softened at 100° and melted at 117–118°. [c] After drying at 77° (2 mm.). [d] Crude product. [e] When mixed with the related derivative of the meta isomer the mixture melted at 85–87°.

extract gave 5.4 g. of *p*-toluenesulfinic acid (18% yield based on *p*-bromotoluene). Evaporation of the ether layer (1) gave 8.0 g. of a yellow solid. Recrystallization from absolute ethanol yielded a small amount of crystalline white solid, m.p. 125-126° (reported[12] for *p,p'*-ditolyl, m.p. 125°). *Anal.* Calcd. for $C_{14}H_{14}$: C, 92.25; H, 7.75. Found: C, 91.86; H, 7.91.

The ethanol filtrate was evaporated to dryness and the residue on recrystallization from *n*-hexane yielded a crystalline white solid, m.p. 93-94° (reported[7] for di-*p*-tolyl sulfoxide, m.p. 95°). *Anal.* Calcd. for $C_{14}H_{14}OS$: C, 73.01; H, 6.13. Found: C, 73.02; H, 6.23.

B. Synthesis of Isomeric Sodium *n*-Dodecylbenzenesulfonates. *p*-Bromolaurophenone (II).—This compound was prepared in 22-54% yield by the general procedure described by Cason.[9] *n*-Hendecylmagnesium bromide was prepared from 117 g. (0.50 mole) of *n*-hendecyl bromide and 12.2 g. (0.50 mole) of magnesium in 300 ml. of ether. The entire reaction was carried out in an atmosphere of dry oxygen-free nitrogen. The reaction mixture was cooled to 0° and 50.4 g. (0.27 mole) of anhydrous cadmium chloride was added over a 5-minute interval. After the addition of 100 ml. of ether, the reaction mixture was refluxed until a negative Color Test I[13] was obtained (3 hours).

The ether was then removed and replaced with 300 ml. of benzene in the conventional manner. To the stirred reaction mixture was added 87.8 g. (0.40 mole) of *p*-bromobenzoyl chloride in 100 ml. of benzene over a one-half-hour period. Gentle heating was applied to maintain reflux. After the final addition the mixture was stirred and refluxed for 3 hours and then hydrolyzed by pouring into 10% sulfuric acid solution and ice. The benzene layer was separated and washed successively with 5% sodium hydroxide solution and water. The solvent was removed and the residue recrystallized from petroleum ether (b.p. 30-60°) to give 73 g. (54% based on the acid chloride) of product, m.p. 59-61°. Further recrystallization brought the melting point up to 62-63°. *Anal.* Calcd. for $C_{18}H_{27}OBr$: C, 63.76; H, 7.96; Br, 23.57. Found: C, 63.5; H, 7.90; Br, 24.2.

A 2,4-dinitrophenylhydrazone, m.p. 114-115°, was prepared. *Anal.* Calcd. for $C_{24}H_{31}N_4O_4Br$: N, 10.79. Found: N, 10.80.

***p*-Bromo-*n*-dodecylbenzene (I).**—*p*-Bromolaurophenone was reduced by the Huang-Minlon variation[10] of the Wolff-Kishner method. However, two modifications were introduced: (1) a large excess of hydrazine was employed and vigorous stirring was maintained throughout the reduction because of the relative insolubility of this phenone in diethylene glycol; (2) less debromination and better yields were observed if the recommended time allowed for hydrazone formation was prolonged before raising the temperature to produce the desired hydrocarbon.

To 52.7 g. (0.16 mole) of *p*-bromolaurophenone in a 1-l. flask equipped with a thermometer and stirrer were added 210 ml. of diethylene glycol, 21 g. of sodium hydroxide, and 50 g. of 85% hydrazine hydrate. This mixture was stirred and heated at approximately 100° for 24 hours. A small aliquot was withdrawn and a negative test for ionic bromide was obtained. Excess hydrazine and water were then removed until the temperature reached 184°. The mixture was stirred at this temperature for 8 hours. After cooling it was poured into water and ether extracted. Bromide ion equivalent to 8% of the original *p*-bromolaurophenone was found in the aqueous layer.

After removal of the ether, the organic residue was distilled from a Claisen flask to give 30.2 g. (60%) of *p*-bromo-*n*-dodecylbenzene, b.p. 190-191° (4 mm.), $n^{20}D$ 1.5034. *Anal.* Calcd. for $C_{18}H_{29}Br$: Br, 24.58; C, 66.50; H, 8.92. Found: Br, 24.7; C, 66.70; H, 8.89.

***p*-*n*-Dodecylbenzenesulfinic Acid (III).**—To a 500-ml. three-neck flask equipped with a reflux condenser, stirrer, and a means of maintaining a positive pressure of pure nitrogen, was added 1.5 g. (0.22 g. atom) of finely divided lithium. The latter had been pounded out into thin strips and then cut with scissors to fall directly into the flask. Over a one-half-hour period, 29.2 g. (0.09 mole) of *p*-bromo-*n*-dodecylbenzene in 120 ml. of dry ether was added to the lithium, after which the mixture was stirred and refluxed for one hour. In a separate experiment the yield of aryllithium intermediate was found to be 75% by direct titration.

The flask was then immersed in an ice-bath and dry sulfur dioxide was passed through the stirred solution for one hour. An additional 100 ml. of dry ether was added during the sulfination. Preliminary experimentation indicated that hydrolysis and extraction resulted in emulsions very difficult to break. Consequently, the reaction mixture was centrifuged and the ether layer decanted from the residue. The latter was washed twice with ether by centrifugation and subsequently dislodged from the centrifuge bottle with dilute acid. This formed a suspension which was extracted with ether. The latter was dried with Drierite, filtered and evaporated to give a 63% yield of crude *p*-*n*-dodecylbenzenesulfinic acid (m.p. 49-51°). The product, recrystallized twice from petroleum ether, was a white powder, m.p. 54-55°, which slowly turned yellow on standing. *Anal.* Calcd. for $C_{18}H_{30}O_2S$: C, 69.68; H, 9.67. Found: C, 70.0; H, 9.64.

Sodium *p*-*n*-Dodecylbenzenesulfonate (IV).—To 17.0 g. (0.055 mole) of *p*-*n*-dodecylbenzenesulfinic acid was added 200 ml. of 2% sodium hydroxide solution and a slight excess of a 4% sodium permanganate solution (peroxide oxidation caused excessive foaming). The temperature was maintained at 35-40° during the oxidation. After standing overnight excess permanganate was reduced with sodium sulfite and the mixture was heated to boiling and filtered hot. The filtrate was neutralized with sulfuric acid and evaporated to dryness. Hot ethanol extraction of the dry salts gave 13.4 g. (70%) of sodium *p*-*n*-dodecylbenzenesulfonate.

***m*-Bromolaurophenone.**—This compound was prepared from *m*-bromobenzoyl chloride and di-*n*-hendecylcadmium as described for (II). The crude ketone was obtained by distillation from a Claisen flask in a nitrogen atmosphere. Those fractions (b.p. 170-200°, 1-2 mm.) which gave a positive ketone test were combined for further purification. The product was separated from a persistent contaminant, *n*-docosane, by dissolution in glacial acetic acid and filtration of the insoluble hydrocarbon. The filtrate was diluted with water and ether extracted. After washing the ether extracts successively with 2% sodium hydroxide solution and water, the ether layer was dried and evaporated. The product was further purified by fractional recrystallization from 2:1 methanol-acetone to give a 20% yield of product, m.p. 25-30°. The sample submitted for analysis melted at 29-30°. *Anal.* Calcd. for $C_{18}H_{27}OBr$: C, 63.76; H, 7.96; Br, 23.57. Found: C, 63.3; H, 7.89; Br, 23.43. The ketone yielded an orange 2,4-dinitrophenylhydrazone, m.p. 103-104°, after drying at 77° (2 mm.). *Anal.* Calcd. for $C_{24}H_{31}N_4O_4Br$: N, 10.79. Found: N, 10.89.

***m*-Bromo-*n*-dodecylbenzene.**—To a mixture of 33.4 g. (0.10 mole) of *m*-bromolaurophenone, 14 g. of sodium hydroxide and 135 ml. of diethylene glycol, was added 32 g. of 85% hydrazine hydrate. The reduction was carried out as described for (I). Bromide ion equivalent to 3% of the

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[12] Mieleitner, *Z. Kryst. Min.*, **55**, 71 (1915).

[13] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

bromophenone was found in the aqueous layer. A 60% yield of crude *m*-bromo-*n*-dodecylbenzene, b.p. 182–192° (3 mm.), was obtained by fractionation through a 15″ Vigreux column. Over 80% of this product boiled between 188–192° (3 mm.), n^{20}D 1.5044. *Anal.* Calcd. for $C_{18}H_{29}Br$: C, 66.50; H, 8.92; Br, 24.58. Found: C, 66.8; H, 9.05; Br, 24.52.

***m*-*n*-Dodecylbenzenesulfinic Acid.**—This compound was prepared in 44% yield from 15.0 g. (0.046 mole) of *m*-bromo-*n*-dodecylbenzene and 0.77 g. (0.11 g. atom) of lithium in the manner described for (III). The yield of the aryllithium intermediate was 78%. The sulfinic acid after two recrystallizations from petroleum ether was a white powder, m.p. 63–64°, which became yellow on standing. *Anal.* Calcd. for $C_{18}H_{30}O_2S$: C, 69.68; H, 9.67. Found: C, 69.80; H, 9.68.

Sodium *m*-*n*-Dodecylbenzenesulfonate.—This compound was prepared in 80% yield from 5.7 g. (0.018 mole) of *m*-*n*-dodecylbenzenesulfinic acid as described for (IV).

***o*-Bromolaurophenone.**—This compound was prepared from *o*-bromobenzoyl chloride and di-*n*-hendecylcadmium as described for (II). The crude ketone was dissolved in 2:1 methanol–acetone, cooled and filtered to remove a small amount of *n*-docosane. The filtrate was evaporated and the residue fractionated through a 15″ Vigreux column under nitrogen to give a 33% yield of product, b.p. 187–189.5° (1–2 mm.), n^{20}D 1.5116. *Anal.* Calcd. for $C_{18}H_{27}OBr$: C, 63.76; H, 7.96; Br, 23.57. Found: C, 63.90; H, 7.98; Br, 23.32.

To obtain a good yield of the 2,4-dinitrophenylhydrazone it was necessary to reflux a mixture of the bromophenone and 2,4-dinitrophenylhydrazine in an acid–ethanol solution overnight. Cooling deposited yellow crystals, which were dissolved in pentane and filtered to remove unreacted reagent. Cooling the filtrate gave yellow crystals, m.p. 68–69°. The product was purified chromatographically to remove an otherwise persistent impurity and dried at 40° (1–2 mm.), m.p. 70–71°. *Anal.* Calcd. for $C_{24}H_{31}N_4O_4Br$: N, 10.79. Found: N, 10.81.

***o*-Bromo-*n*-dodecylbenzene.**—To a mixture of 53.4 g. (0.16 mole) of *o*-bromolaurophenone, 21 g. of sodium hydroxide and 205 ml. of diethyleneglycol was added 50 g. of 85% hydrazine hydrate. The reduction was carried out as described for (I). Bromide ion equivalent to 15% of the bromophenone was found in the aqueous layer. The crude product was fractionated through a 15″ Vigreux column under nitrogen to give 26.5 g. (52%) of *o*-bromo-*n*-dodecylbenzene, b.p. 174–176° (2 mm.), n^{20}D 1.5060. *Anal.* Calcd. for $C_{18}H_{29}Br$: C, 66.50; H, 8.92; Br, 24.58. Found: C, 66.65; H, 8.72; Br, 24.3.

Sodium *o*-*n*-Dodecylbenzenesulfonate.—To 1.0 g. (0.14 g. atom) of finely divided lithium was added 17 g. (0.052 mole) of *o*-bromo-*n*-dodecylbenzene in 80 ml. of dry ether. In a separate experiment the yield of the aryllithium intermediate was found to be 90%. Sulfination in the usual manner failed to precipitate the desired lithium sulfinate. However, when a small sample was withdrawn from the reaction mixture and the solvent and sulfur dioxide removed under nitrogen, the residue was found to be neutral on hydrolysis. With another sample treated similarly a negative Color Test I[13] was observed.

The diethyl ether was evaporated from the reaction mixture and replaced by petroleum ether, 30–60°. A white solid which proved to be lithium bromide settled out immediately and was filtered. The filtrate slowly became turbid on standing at room temperature and a brown gelatinous solid collected after two hours. This crude lithium sulfinate, separated and washed by centrifugation, weighed 6.7 g. (41%) after drying. The petroleum ether layer (I) was reserved.

Four grams of this product was oxidized with sodium permanganate as described for (IV) to give 1.7 g. (38% based on the lithium sulfinate) of crude sodium *o*-*n*-dodecylbenzenesulfonate.

The petroleum ether layer (I) was evaporated and dried under reduced pressure. The residue weighed 8.0 g. It was insoluble in base, and gave a positive test for sulfur and a weak test for bromine. It had a very small ash.

This material was thought to be the thioester (resulting from a disproportionation) and/or the sulfoxide. Accordingly, 2.7 g. of this residue was treated with 0.8 g. of potassium permanganate dissolved in hot glacial acetic acid in an attempt to oxidize any ester present to the sulfonic acid. After standing for several hours the excess acetic acid was removed by gentle heating under vacuum. The residue was boiled with water, treated with Norite and filtered. The filtrate was neutralized and evaporated to dryness. This residue was extracted with ethanol to give 0.39 g. of a thick yellow oil. The latter did give a flame test for sodium and the ash contained sulfate ion. However, no S-benzylthiuronium derivative would form. Further work on this material was discontinued.

Sodium *p*-Lauroylbenzenesulfonate.—A mixture of 20.0 g. (0.059 mole) of *p*-bromolaurophenone, 50 g. of sodium sulfite, 2 g. of cupric sulfate and 500 ml. of water was shaken in a 1-l. iron autoclave for four days at 180° followed by two days at 220°. After cooling, the contents were emptied and filtered. The insoluble material was extracted with ether to recover 7.0 g. (0.021 mole) of unreacted *p*-bromolaurophenone. The residue after ether extraction was recrystallized from hot ethanol to give 6.1 g. of sodium *p*-lauroylbenzenesulfonate. This is a 29% conversion based on the amount of phenone charged. *Anal.* Calcd. for $C_{18}H_{27}O_4SNa$: Na, 6.35. Found: Na, 6.27. The product yielded an S-benzylthiuronium derivative, m.p. 166–167°, after drying at 77° (2 mm.). *Anal.* Calcd. for $C_{26}H_{38}O_4S_2N_2$: N, 5.53. Found: N, 5.54.

Reduction of Sodium *p*-Lauroylbenzenesulfonate by the Clemmensen Method.—Five grams (0.014 mole) of sodium *p*-lauroylbenzenesulfonate was reduced with 20 g. of amalgamated zinc, 25 ml. of concentrated hydrochloric acid, 5 ml. of glacial acetic acid and 20 ml. of water. After refluxing for 20 hours the mixture was decanted from the zinc and evaporated to dryness under an air jet. The residue was dissolved in hot ethanol and then cooled to give the crude zinc sulfonate relatively free of zinc chloride. The crude product was digested with dilute sodium carbonate solution and filtered. After neutralization, the filtrate was evaporated to dryness. Hot ethanol extraction of the residue gave two grams of crude sodium *p*-*n*-dodecylbenzenesulfonate from which an S-benzylthiuronium derivative was made. After repeated recrystallizations and drying it melted at 113°. When mixed with an authentic sample of S-benzylthiuronium *p*-*n*-dodecylbenzenesulfonate (m.p. 117–118°) prepared from IV the melting point was 114–118°.

Acknowledgment.—This work was supported by a grant from The Procter and Gamble Company, to whom we are greatly indebted.

Summary

1. The conversion of an aryl bromide or chloride to the salt of the corresponding sulfonic acid has been accomplished by preparing the aryllithium compound, sulfinating it, and then oxidizing the sulfinic acid to the desired product. This method is to be preferred in some cases over the use of the Grignard intermediate in this type of synthesis.

2. The following new compounds and/or their derivatives are described: *o*-, *m*- and *p*-bromolaurophenones; *o*-, *m*- and *p*-bromo-*n*-dodecylbenzenes; *o*-, *m*- and *p*-*n*-dodecylbenzenesulfinic acids; *o*-, *m*- and *p*-*n*-dodecylbenzenesulfonic acids; and sodium *p*-lauroylbenzenesulfonate.

LAFAYETTE, INDIANA

RECEIVED JUNE 12, 1950