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LITHIUM ALUMINUM HYDRIDE REDUCTION OF CERTAIN SULFONIC ACID DERIVATIVES

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The importance of lithium aluminum hydride as a highly selective reducing agent has been demonstrated by Nystrom and Brown (1) and subsequently by numerous others. At the outset of the present work its application to the reduction of organic sulfur compounds had not been reported, although reductions have since been described of sulfonic esters (2, 3), disulfides (3, 4), sulfonyl chlorides (3, 5), sulfones (6), and miscellaneous other types (3). This paper, which is concerned with the reduction of certain sulfonyl halide, anhydride, and amide derivatives of sulfonic acids, provides an extension and modification of published information with respect to products, stoichiometry, and mechanism.

Early experiments in this laboratory in the reduction of *p*-toluenesulfonyl chloride with lithium aluminum hydride in ether at the reflux temperature gave *p*-toluenesulfinic acid in 63–77% yield. This reduction has been reported to give rise to thiols (3, 5) although sulfinic acids have been isolated after the reduction of sulfonic esters (2), and tentatively identified after reduction of a disulfonyl chloride (7). The proportion of hydride used in our experiments was smaller than that used by others, suggesting that the sulfinic acid is an early product in a series of steps leading to the thiol.

It was possible to avoid partial reduction beyond the sulfinic acid stage and thus improve the yield by "inverse" addition of the hydride to the halide at lower temperatures in a technique similar to that useful in Grignard reactions (8). Reduction was very slow at temperatures much below −20°, but proceeded smoothly at this temperature to give *p*-toluenesulfinic acid in 93% yield. Pure products were isolated in this reduction and in other types described later by a separation procedure based on the difference in acidity of sulfinic acids, thiols, and disulfides.

A study of the stoichiometry of the reduction gave results consistent with the equation

$$2\ C_7H_7SO_2Cl + LiAlH_4 \rightarrow (C_7H_7SO_2)_2LiAlCl_2 + 2\ H_2.$$

Consumption of the sulfonyl halide was determined by isolation of the small unreacted portion, and that of the hydride by measurement of the hydrogen evolved on acidification before and after reduction. The sulfinic acid was determined by isolation after acidification of the salt formed in the reaction; this salt was not characterized and need not have the precise composition ascribed to it. Calculation of the results to a basis of two moles of sulfonyl chloride gave mole ratios of 1.00, 1.86, and 2.14 for the hydride, sulfinic acid, and hydrogen, respectively.

The reduction of benzenesulfonyl chloride proceeded rapidly at −65° giving

benzenesulfinic acid in 89% yield. On the basis of two moles of benzenesulfonyl chloride, the mole ratios were 1.02, 1.78, and 2.02 for the hydride, sulfinic acid, and hydrogen, respectively.

The greater ease of reduction of benzenesulfonyl chloride suggests that the mechanism of reduction involves a nucleophilic attack by complex hydride ions such as AlH_4^-. The attack must differ, however, from the nucleophilic displacement on carbon probable for compounds containing carbon attached to oxygen, nitrogen, or halogen (9) since this would lead to a hydrocarbon [*cf.* (4)]. A possible mechanism for the sulfonyl chloride reduction involves the nucleophilic displacement of chloride ion from the sulfur atom by a complex hydride ion, followed by attack of a complex hydride ion on the hydrogen of the resulting sulfinic acid with the formation of a sulfinate salt and hydrogen.

$$RSO_2Cl \xrightarrow{AlH_4^-} RSO_2H + Cl^- \xrightarrow{AlH_4^-} RSO_2^- + H_2$$

Alternatively, the entire reaction may occur by a similar but concerted process in which an unstable intermediate formed from the sulfonyl chloride and complex hydride ion gives the products in only one step.

A principal advantage of lithium aluminum hydride as a reducing agent lies in its ability to reduce a functional group without attack on a double bond in the molecule. The reduction of cinnamaldehyde using the normal procedure, however, gives hydrocinnamyl alcohol (10). Reduction of a double bond adjacent to a functional group also occurs in other instances (*e.g.* with —COR, —CO_2H, —NO_2, etc.). If, on the other hand, cinnamaldehyde is reduced by inverse addition of the hydride below 10°, cinnamyl alcohol is obtained (10); similarly, a substituted cinnamic ester has been reduced at −10° to the corresponding substituted cinnamyl alcohol (26). It was therefore of interest to determine whether or not the double bond could be preserved in the reduction of the analogous sulfonyl chloride. The reduction of β-styrenesulfonyl chloride was accordingly carried out by adding the hydride to it at −70°. β-Styrenesulfinic acid was isolated as the sodium salt in 78% yield.

In the reduction of methanesulfonyl chloride at −70°, 85–90% of the amount of hydrogen corresponding to reduction to the methanesulfinate salt was evolved. An attempt was made to isolate the silver salt by treating an ether extract of the acidified reaction mixture with ammonium hydroxide followed by silver nitrate, but only small amounts of a salt were obtained which could not be derivatized as the sulfone. Inasmuch as the difficulty may have been largely one of isolation, higher homologs may give more satisfactory results.

p-Toluenesulfonyl chloride has been reduced to *p*-thiocresol in 50% yield by Marvel and Caesar (5), the stoichiometry being assumed that shown by the equation

$$2\ RSO_2Cl + 3\ LiAlH_4 \rightarrow LiAlCl_2(SR)_2 + 6\ H_2 + 2\ LiAlO_2.$$

In carrying out the reduction in this laboratory, a 62% excess of the hydride was added inversely to a boiling ether solution of the chloride. On the basis of two moles of the sulfonyl chloride, the mole ratios were 2.84 for the hydride, 1.78

(89% yield) for *p*-thiocresol, and 5.66 for hydrogen, thus confirming the proposal of Marvel and Caesar.

In preliminary experiments, a 42% excess of hydride resulted in an 83% yield, and a 23% excess in only a 71% yield. Since Strating and Backer (3) reported a reduction in 90% yield using no excess of hydride, it seemed worthwhile to attempt confirmation of this result. A careful attempt to do so resulted in a 90% yield, but of impure product melting over a 43° range, probably because of the presence of the sulfinic acid and disulfide. Pure *p*-thiocresol could not be obtained by the reported procedure of recrystallization. A difference in the composition of the hydride samples used might be responsible for the difference in results.

Strating and Backer (3) stated that the much less rapid reduction of disulfides than of sulfonyl chlorides to thiols contravened the possibility that disulfides were intermediates in the reduction of sulfonyl chlorides to thiols. Sulfinic acids were also said to be excluded as intermediates since in their experience they were reduced to disulfides.

We have obtained diphenyl disulfide, however, in 37% yield by addition of benzenesulfonyl chloride to an amount of hydride insufficient to reduce it completely to thiophenol but more than sufficient to reduce it to the sulfinic acid salt. Di-*p*-tolyl disulfide was isolated after a similar reduction of *p*-toluenesulfonyl chloride (25% yield). The isolation both of disulfides and sulfinic acids serves as presumptive evidence for their function as intermediates in the reduction of sulfonyl halides to thiols, but it is also clearly possible that they are formed in a separate reaction unrelated to thiol formation.

The rapid reduction of the *p*-toluenesulfinic acid salt, preformed at −20°, to *p*-thiocresol in 85% yield upon heating with excess hydride showed that the sulfinic acid salt is not stable once formed, and may therefore be an intermediate in the reduction to the thiol. The mechanism of reduction of the sulfinate to the thiol probably resembles that of the reduction of sulfones to sulfides (6).[1]

The basis for the conclusion of Strating and Backer as to the slow rate of disulfide reduction is not entirely clear, as they were able to reduce di-*p*-tolyl disulfide in 15 minutes in boiling ether (although sterically hindered disulfides were reduced very slowly). In order to determine qualitatively whether the reduction of the disulfide to *p*-thiocresol is slower than that of *p*-toluenesulfonyl chloride by a considerable amount, we subjected the disulfide to conditions approximating those of our sulfonyl chloride reduction. Although the disulfide reduction was complete in only seven minutes as compared with about 35 for the chloride this result does not definitely establish the relative rates because the hydride was not added in one portion owing to the vigor of the reactions; one can conclude only that both reactions are quite rapid. The result is not inconsistent, however, with the possibility that the disulfide is an intermediate, although final decision must await the availability of quantitative data.

Several competing paths may be involved in the reduction of sulfonyl halides

[1] We are indebted to Professor Bordwell for providing us with a copy of this manuscript in advance of publication.

to thiols. Two which appear to be possible in the light of present information are: (A) Formation of a sulfinate salt and its direct reduction by excess hydride. (B) Reaction of the sulfonyl chloride with the sulfinate salt giving a disulfone or with a metal mercaptide giving a thiolsulfonate, either of which are reducible to a disulfide (3), followed by the reduction of the disulfide to the thiol.

Sulfonic anhydrides have not been reduced previously with lithium aluminum hydride. Benzenesulfonic anhydride was found to behave in much the same way as benzenesulfonyl chloride, giving either benzenesulfinic acid in 63% yield or thiophenol in 100% yield depending on the conditions.

Attempts to reduce sulfonamides with the hydride have hitherto been unsuccessful (3, 7), although apparently only unsubstituted sulfonamides have been studied. The refractory behavior of the unsubstituted compounds might arise from the resistance of the rapidly formed anion RSO_2NH^- to further attack by a negatively charged hydride anion. Reduction in this laboratory of N-diethylbenzenesulfonamide, which cannot form such an anion, resulted in the formation of benzenesulfinic acid (57%) and thiophenol (10%). The reason for the very slow reaction of this compound (7 days in boiling tetrahydrofuran) is not evident, but may be the result of Lewis-type salt formation between the sulfonamide nitrogen and a form of an aluminum hydride ion [*cf.* (11)]. The isolation of the sulfinic acid was unexpected in view of the demonstrated ease of reduction of a sulfinate salt.

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EXPERIMENTAL[2]

Preparation and assay of lithium aluminum hydride solution. In a typical preparation, 110.4 g. of lithium aluminum hydride (90–95%, Metal Hydrides, Inc., Beverly, Mass.) was quickly broken up and heated under reflux with 1100 ml. of absolute ether for two days. The resulting suspension was allowed to stand for several days, and the nearly clear supernatant solution was separated from insoluble solid by pumping under dry nitrogen. All equipment used here and subsequently was dried at 110°, assembled while hot, and protected by tubes containing phosphorus pentoxide and calcium oxide.

The assay procedure was based on an unpublished method recommended by Metal Hydrides, Inc. A 2-ml. sample of stock solution was delivered from an Ostwald-Folin pipette into a 125-ml. flask having a side-arm fitted with a soft rubber stopper. The flask was gently swirled while ether was removed using an aspirator connected through a drying-tube and a three-way stopcock. The flask was then connected to a gas burette through two traps cooled with Dry Ice, and 10 ml. of dry dioxane (12) followed by 10 ml. of a mixture (1:1) of dioxane and 95% alcohol was added from a hypodermic syringe the needle of which was inserted through the stopper; a soft stopper is sufficiently self-sealing to permit insertion and withdrawal of the hypodermic needle without leakage. After no further reaction occurred, 10 ml. of 10% sulfuric acid was added from the hypodermic, and the flask was allowed to reach room temperature before reading the volume of gas. The concentration of the solution was calculated from the volume of hydrogen measured, 1 mole of hydride being

[2] All melting points were taken with a calibrated partial immersion thermometer (A.S.T.M. specification) and are corrected. Analyses are by Clark Microanalytical Laboratory, Urbana, Ill.

equivalent to 4 moles of evolved hydrogen. Consecutive assay values differed by less than 2% and remained valid for several weeks.

General procedure for reduction and isolation of products. The reaction vessel was a 500-ml. two-necked Erlenmeyer flask provided with a condenser, in which a thermometer was suspended when required, which was connected through a Drierite tube and traps cooled with Dry Ice to a gas burette which was cooled with ice water. The vertical joint of the flask was fitted with a dropping funnel. Vigorous stirring was provided in all reductions by a magnet sealed in glass and a heavy-duty magnetic stirrer. Heating with a Glas-Col mantle permitted magnetic stirring, and cooling was achieved with solvent in a porcelain vessel to which Dry Ice was added as needed.

Absolute ether required as a solvent was distilled from the hydride into the chilled reaction flask; a portion of this ether was removed for diluting the stock solution to the specified concentration.

Excess hydride remaining after reactions was decomposed by addition of alcohol-ether or water, followed by 10 ml. of 10% sulfuric acid. After the hydrogen thus evolved had been measured, an excess of 10–20% sulfuric or hydrochloric acid was added to dissolve the precipitate. The organic layer was separated, transferred to a fresh separatory-funnel, and extracted with a 5–10% aqueous sodium hydroxide solution. The ether solution was dried over sodium sulfate and concentrated to give the "neutral fraction." The aqueous layer was acidified to about *p*H 5–6 with 1 *N* hydrochloric acid and extracted with ether; concentration of the dried extract gave the "thiol fraction." The "acid fraction" was obtained by further acidification of the aqueous solution to about *p*H 1 with concentrated hydrochloric acid followed by ether extraction. After this extraction was partly complete, the aqueous layer was usually saturated with salt to permit more complete removal of the sulfinic acids. The dried extract was concentrated under reduced pressure with careful warming to obviate decomposition of the sulfinic acids.

Reduction of sulfonyl chlorides to sulfinic acids. (*a*) *p-Toluenesulfonyl chloride.* A solution of 0.0678 mole of hydride in 85 ml. of ether was added dropwise during 2½ hours to a solution of 22.4 g. (0.118 mole) of *p*-toluenesulfonyl chloride, purified by the method of Fieser (13), in 200 ml. of ether while the temperature was maintained at −20°. During the reduction 0.119 mole of hydrogen was evolved. Hydrolysis of excess hydride liberated 0.0504 mole of hydrogen. A neutral fraction consisting of 1.26 g. (0.0066 mole, 6% recovery) of *p*-toluenesulfonyl chloride was obtained, which after recrystallization from benzene had m.p. and mixture m.p. 66–68°. No *p*-thiocresol was present in the thiol fraction.

The acid fraction contained 16.1 g. (93%, based on sulfonyl chloride consumed) of *p*-toluenesulfinic acid, m.p. 76–80°, neutral equivalent 157.5 (Calc'd 156). After recrystallization from water the m.p. was 81–83° undepressed by an authentic sample made from the sodium salt prepared by a modification of a reported method (14); reported m.p. 84° (15). The acid (3.5 g.) was converted to methyl *p*-tolyl sulfone by treatment with 2.24 g. of sodium carbonate in 20 ml. of water, evaporation to dryness, leaching the sodium salt with boiling alcohol, and then following the procedure of Otto (16). After recrystallization from aqueous ethanol, the yield was 75%, m.p. and mixture m.p. with authentic sulfone, 86–87°; reported m.p. 86–87° (16).

(*b*) *Benzenesulfonyl chloride.* A solution of 0.0730 mole of hydride in 85 ml. of ether was added dropwise during 1½ hours to 20.4 g. (0.116 mole) of redistilled benzenesulfonyl chloride in 200 ml. of ether at about −65°. During the reduction 0.116 mole of hydrogen was evolved, and 0.057 mole was liberated upon decomposition of excess hydride.

The neutral fraction contained 0.47 g. of an unidentified oil. No thiophenol was isolated. The acid fraction consisted of 14.6 g. (89%) of benzenesulfinic acid, m.p. 74.5–76°, undepressed by an authentic sample made from the sodium salt which was prepared by a modification of a reported method (17); reported m.p. 83° (15). A portion of this product was converted to methyl phenyl sulfone (18) in 55% yield after recrystallization from aqueous alcohol; m.p. 86.5–87.5°, undepressed by an authentic sample; reported m.p. 88° (18).

(*c*) *β-Styrenesulfonyl chloride.* Ammonium β-styrenesulfonate, prepared from styrene

and sulfamic acid (19), was converted to the sodium salt which upon treatment with phosphorus pentachloride (20) gave β-styrenesulfonyl chloride. Purification with Darco and recrystallization from Skellysolve B gave material of m.p. 89–90.5°; reported m.p. 89–89.5° (20).

A solution of 14.2 g. of β-styrenesulfonyl chloride in 150 ml. of ether was cooled to −70° and maintained at about this temperature while 0.055 mole of hydride in 50 ml. of ether was added dropwise during 2½ hours. At about −70° β-styrenesulfonyl chloride is sparingly soluble in ether, but this caused no difficulty and served to moderate the reaction. After decomposition of the excess hydride and solution of the precipitate in the usual way, the ether layer was extracted with 7.5 g. of sodium carbonate in 70 ml. of water, and then with a 10% sodium hydroxide solution which removed 0.27 g. of an intractable crude material. The ether fraction consisted of 2.3 g. of what appeared to be impure sulfonyl chloride.

The carbonate extract was evaporated to dryness under reduced pressure, and the residue of 15.9 g. was boiled with several portions of alcohol. The extract after being filtered while hot and evaporated to dryness gave 10.4 g. (78%) of sodium β-styrenesulfinate, which after recrystallization from *n*-propyl alcohol gave small white crystals.

Anal. Calc'd for $C_8H_7NaO_2S$: S, 16.86. Found: S, 16.48.

The sulfinate salt was converted to β-styryl 2,4-dinitrophenyl sulfone in 85% yield (21). Recrystallization from benzene gave material having the constant m.p. 165.5–167°, about 8° higher than the reported m.p. (21); possibly the two values correspond to different geometrical isomers. An acetone solution of the sulfone rapidly decolorized an aqueous potassium permanganate solution.

Anal. Calc'd for $C_{14}H_{10}N_2O_6S$: C, 50.30; H, 3.02.
Found: C, 50.42; H, 3.17.

Reduction of p-toluenesulfonyl chloride to p-thiocresol. In an attempt to duplicate the result of Strating and Backer (3), a solution of 0.076 mole of hydride in 190 ml. of ether was added dropwise during 35 minutes to a solution of 9.6 g. of *p*-toluenesulfonyl chloride in 100 ml. of ether, and stirring was continued for one hour longer until hydrogen evolution ceased. Excess hydride was hydrolyzed, and the precipitate was dissolved with 130 ml. of 2 *N* hydrochloric acid. The ether layer was washed with water, dried, and concentrated under reduced pressure to 5.90 g. of solid, m.p. 38–81°. Attempted purification by recrystallization from aqueous alcohol as suggested by Strating and Backer gave about 3 g. of solid which liquefied at room temperature; a repetition of the recrystallization likewise proved ineffective.

Better results were obtained in the reduction by the dropwise addition during 35 minutes of 0.125 mole of hydride in 55 ml. of ether to 9.8 g. (0.0514 mole) of *p*-toluenesulfonyl chloride in 100 ml. of ether at the reflux temperature. Stirring under reflux was then continued for four hours. A total hydrogen volume amounting to 0.145 mole was evolved during the reduction. The volume evolved during the addition alone was not determined, but only very little more appeared during the period of reflux; it accordingly appears that the reaction was largely complete in approximately 35 minutes. An additional 0.206 mole of hydrogen was evolved upon hydrolysis of excess hydride. The thiol fraction contained 5.7 g. (89%) of *p*-thiocresol which without further purification had m.p. and mixture m.p. 41–42°. Conversion of a portion of the product to *p*-tolyl 2,4-dinitrophenyl sulfide (22) gave a 57% yield after recrystallization from absolute alcohol, m.p. 102.5–103.5°; reported m.p. 103°. The acid fraction contained 0.53 g. (7%) of *p*-toluenesulfinic acid, m.p. and mixture m.p. with authentic material, 77–78.5°.

Reduction of the p-toluenesulfinate salt complex to p-thiocresol. A solution of 0.107 mole of the hydride in 104 ml. of ether was added during 2½ hours to 9.8 g. (0.0514 mole) of *p*-toluenesulfonyl chloride in 200 ml. of ether at −20°; 0.0706 mole of hydrogen was evolved (37% in excess of that expected for reduction to the sulfinate alone, but very much less than the 0.154 mole indicating complete reduction to the thiol). On warming the mixture to the reflux temperature during about 20 minutes a considerable volume of hydrogen was evolved. Very little more appeared when the mixture was stirred under gentle reflux for

five hours, indicating that the reaction was complete in about 20 minutes. The thiol fraction consisted of 5.44 g. (85%) of *p*-thiocresol, m.p. 42.5–43.5°, undepressed by authentic material, and the acid fraction contained 0.88 g. (11%) of *p*-toluenesulfinic acid, m.p. 77–79°, undepressed by an authentic sample.

Reduction of benzenesulfonyl chloride to diphenyl disulfide. A solution of 10.95 g. (0.062 mole) of benzenesulfonyl chloride in 50 ml. of ether was added to 0.067 mole of the hydride in 25 ml. of ether at a rate sufficiently rapid to cause refluxing. The mixture was then stirred 45 minutes. The acid fraction contained 4.18 g. (48%) of benzenesulfinic acid, m.p. 75–78°. The neutral fraction consisted of 2.47 g. (37%) of diphenyl disulfide, m.p. 54–57°, which after recrystallization from alcohol melted at 59.5–60.5°, undepressed by authentic material (23); reported m.p. 59–60°.

Reduction of di-p-tolyl disulfide to p-thiocresol. Di-*p*-tolyl disulfide was prepared by a modification of a method for diphenyl disulfide (23) better adapted to preparation in quantity. Bromine (40–50 g.) was added to 55 g. of *p*-thiocresol in 300 ml. of 10% potassium hydroxide with vigorous stirring during two hours until no further precipitate appeared. Recrystallization from alcohol gave 43.5 g. (80%) of solid, m.p. 43.5–44.5°, which after a second recrystallization amounted to 33.2 g. (61%), m.p. 45–45.5°; reported m.p. 45–46° (24).

For reduction, 0.107 mole of the hydride in 44 ml. of ether was added dropwise to 6.32 g. of the disulfide in 100 ml. of ether; the heat of reaction caused refluxing of the ether. The reaction went to completion (no appreciable further evolution of hydrogen) in about seven minutes before more than one-fifth of the hydride had been added. The sole product isolated was 5.45 g. (86%) of *p*-thiocresol, m.p. and mixture m.p. with authentic material, 42.5–43.5°.

Reduction of benzenesulfonic anhydride. (*a*) *To benzenesulfinic acid.* A solution of 0.017 mole of the hydride in 18 ml. of ether was added dropwise during two hours to 8.21 g. of benzenesulfonic anhydride (m.p. 76–90°; prepared by a method to be described elsewhere) in 100 ml. of ether, while the temperature was maintained at −70°. The acid fraction consisted of 2.45 g. (63%) of benzenesulfinic acid, m.p. 75–77.5°, undepressed by an authentic sample. The neutral fraction contained 0.97 g. of an oil which could not be crystallized, and the thiol fraction a trace of thiophenol.

(*b*) *To thiophenol.* A solution of 0.044 mole of the hydride in 18 ml. of ether was added during one-half hour to 6.62 g. of benzenesulfonic anhydride in 100 ml. of ether at the reflux temperature. The mixture was then stirred under reflux for another hour; yield, 2.47 g. (100%) of thiophenol, n_D^{25} 1.5805; reported $n_D^{23.2}$ 1.5861 (25). A portion of the thiophenol was converted to phenyl 2,4-dinitrophenyl sulfide (22) in 74% yield; m.p. 119–120.5° (reported m.p. 121°).

Reduction of N-diethylbenzenesulfonamide. We are indebted to the Wyandotte Chemicals Corp. for a sample of N-diethylbenzenesulfonamide which we purified by distillation, and to the Electrochemical Division of the du Pont Co. for one of tetrahydrofuran, which was treated with sodium hydroxide pellets (4), refluxed over sodium, and distilled.

A solution of 0.104 mole of the hydride in 50 ml. of ether was diluted with 100 ml. of tetrahydrofuran and the ether was removed until the vapor temperature was 65°. Then 10.9 g. (0.051 mole) of N-diethylbenzenesulfonamide in 200 ml. of tetrahydrofuran was added, and the mixture stirred at the reflux temperature for seven days (hydrogen evolved, 0.055 mole). Complete reduction would require 0.051 mole based upon the equation

$$2\ C_6H_5SO_2N(C_2H_5)_2 + LiAlH_4 \rightarrow (C_6H_5SO_2)_2LiAl[N(C_2H_5)_2]_2 + 2\ H_2.$$

The acid fraction consisted of 4.22 g. (57%) of benzenesulfinic acid, m.p. 78.5–80°, undepressed by an authentic sample. The thiol fraction comprised 0.56 g. (10%) of crude thiophenol which was converted to phenyl 2,4-dinitrophenylsulfide in 41% yield after recrystallization from absolute alcohol; m.p. 120–121°.

A volatile water-soluble amine, presumably diethylamine, was present in the acid hydrolyzate after neutralization.

Benzenesulfinic acid was obtained in 43% yield and 33% of unchanged sulfonamide was recovered after a reduction period of 18 hours when about 0.1 mole of the amide in 100 ml. of solvent was used. The bulky precipitate made stirring difficult at this concentration, however, and on two occasions a portion of the precipitate decomposed with moderate violence when the magnetic stirrer failed.

SUMMARY

Benzenesulfonyl chloride and *p*-toluenesulfonyl chloride are reduced in high yield with lithium aluminum hydride either to sulfinic acids or to thiols, depending upon the conditions used. The stoichiometry of the reactions is given, and evidence bearing upon the mechanism of reduction discussed. Sodium β-styrenesulfinate was obtained by reduction of β-styrenesulfonyl chloride.

N-Diethylbenzenesulfonamide is reduced to benzenesulfinic acid and thiophenol, and benzenesulfonic anhydride to either thiophenol or benzenesulfinic acid.

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