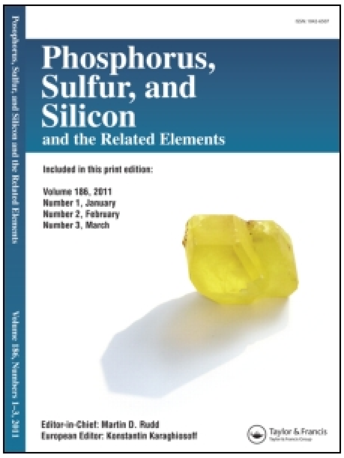

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# HYDROLYTIC DESULFONATION OF CERTAIN AMINOBENZENESULFONIC ACIDS

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# HYDROLYTIC DESULFONATION OF CERTAIN AMINOBENZENESULFONIC ACIDS

by

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Hydrolytic desulfonation, a general procedure for the replacement of an aromatic sulfonic group by a proton, has wide scientific and commercial utility:[1]

$$RSO_2OH + H_2O \xrightarrow{H^+} RH + H_2SO_4$$

Although the effect of various substituents on the relative ease of desulfonation has been studied fairly extensively, that of the amino group has received only limited consideration. This approach has been used commercially for preparing several amino-naphthalene and anthraquinone dye intermediates.[1] 2- And 4-aminobenzenesulfonic acids can be desulfonated in good yield, as can also 3-nitro-4-amino-[2] and 3,5-dinitro-4-aminobenzenesulfonic[3] acids. 3-Aminobenzenesulfonic acid gave no product,[1] and in fact we have noted no published example of the acid-catalyzed hydrolytic removal of a sulfonic group *meta*-oriented to an amino group.[4] It is noteworthy in this connection that the hydrolysis of 2-aminobenzene-1,4-disulfonic acid stops with the formation of 3-aminobenzenesulfonic acid.[5]

We report herein the first examples of the acid-catalyzed desulfonation of 3-aminobenzenesulfonic acids, of diaminobenzenesulfonic acids, and of benzenesulfonic acids substituted by both amino and methyl groups.[6]

The data are summarized in Table I. It is noted that 3-aminobenzenesulfonic acid **1**, in agreement with the literature,[1] did not undergo desulfonation. However, when the ring was additionally substituted by a methyl group *ortho* **3**, or *para* **2**, to the sulfonic group, desulfonation did occur, although the yields were poor and unreacted starting material was recovered. Better yields were obtained when the amino groups were either *ortho* or *para* to the sulfonic group (**4** and **5**). The compounds with two amino groups *ortho* and *para* to the sulfonic group (**6** and **7**) gave good yields at lower temperatures and at shorter times of reaction. These results are all consistent with the earlier conclusion[1] that electron-donating groups *ortho* or *para* to the sulfonic group facilitate hydrolytic desulfonation.

TABLE I[a]

| Compound no. | Substituents in benzenesulfonic acid | $F_3CSO_2OH$ Temp.[b] | $F_3CSO_2OH$ Yield[c] | $H_3PO_4$ Temp. | $H_3PO_4$ Yield | 65% $H_2SO_4$ Temp. | 65% $H_2SO_4$ Yield |
|---|---|---|---|---|---|---|---|
| 1 | 3-Amino | 220 | 0 | 245[d] (4 hr) | 0 | – | – |
| 2 | 3-Amino-4-methyl | 215 | 18[e] | 210 | 0 | – | – |
| 3 | 3-Amino-6-methyl | 215 | 26 | 210 | 12[f] | – | – |
| 4 | 2-Amino-5-methyl | 170 | 84 | 195 | 74 | 185[g] | 50 |
| 5 | 4-Amino-5-methyl | 190 | 45 | 210 | 20 | – | – |
| 6 | 2,4-Diamino | 160 (3 hr) | 77 | – | – | 155 | 89 |
| 7 | 2,4-Diamino-5-methyl | 155 (1 hr) | 91 | 155 (1 hr) | 50 | 155 | 90 |

[a] Conditions were not optimized; all runs 7 hr except as shown.

[b] All temperatures are ± 5°.

[c] All yields are mole % based on sulfonic acid reacted.

[d] Decomposition was noted after 4 hrs.

[e] Twenty-five % of starting compound recovered.

[f] Sixty-four % of starting compound recovered.

[g] Seventy-five % used; 65% acid gave no reaction in 7 hr at 150°.

It is noted that trifluoromethanesulfonic acid gave better yields than phosphoric, especially in one case 2 where the latter acid gave no amine. This result is consistent with a conclusion drawn from our previous study[7] to the effect that this acid is more effective than phosphoric for desulfonating other types of sulfonic acids. As noted below, it is also more convenient to use with respect to recovery of the amine from the reaction mixture.

## Experimental Section

The sulfonic acids were purchased from commercial sources, except for 7, which was supplied by the courtesy of Mr. George F. Lisk, Specialty Chemicals Div., Allied Chemical Corp., Buffalo, N.Y. Compounds **4**, **6**, and **7** were recrystallized from water; the other compounds were used as received.

The sulfonic acid (0.05 mol), trifluoromethanesulfonic acid (25 ml), and water (10 ml) were mixed in a flask equipped for distillation and provided with a magnetic stirrer. The mixture was heated with stirring, and distilled to the desired reaction temperature, at which point distillation was discontinued and the mixture was refluxed under the conditions indicated in Table I. The reaction mixture was cooled, diluted with 100 ml water, and allowed to stand overnight for separation of any unreacted starting material, which was filtered, washed with water, dried, and identified by its ir spectrum. The solution was made strongly alkaline with sodium hydroxide, and extracted with ethyl ether for recovery of the amine, which was identified by melting point and ir spectrum.

Desulfonations with phosphoric acid were affected similarly with the sulfonic acid (0.05 mol) and 85% phosphoric acid (40 g). The mixture was distilled to the reaction temperature, refluxed, diluted, and filtered for recovery of unreacted starting material as indicated above. However, it was found necessary to reflux the alkaline solution for about 30 minutes to liberate all the amine, and to dilute the cooled hydrolysate substantially to avoid troublesome crystallization of phosphate salts during ether extraction.

No distillation step was required when using 65% sulfuric acid (100 g per 0.05 mol sulfonic acid). It was noted (for **6** and **7**) that the diamine sulfates slowly crystallized at 10° from the hydrolysate; they could be recovered in good yield by filtration as free-flowing, non-hygroscopic solids This operation considerably facilitates isolation of the amine and permits reuse of the filtrate acid for subsequent hydrolyses if desired.

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