SHORT PAPER

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A study on the sulfonation of aromatic amines with sulfuric acid under microwave irradiation

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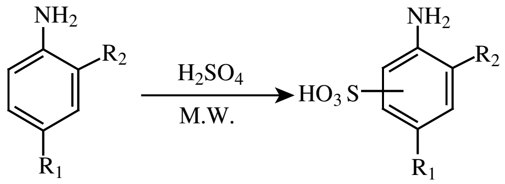
The sulfonation of aromatic amines with high yields, simple operations and short reaction time has been studied under microwave irradiation in solvent-free conditions.

Keywords: aromatic amines, sulfonic acids

The amino aromatic sulfonic acids are of importance as intermediate to prepare drugs, dyes and pigments.[1] There are some methods reported to synthesise these compounds, such as ammonolysis of aromatic sulfonic acids and the direct sulfonation of aromatic amines[2] *etc*. The latter method is more common than the former one. The sulfonating agents include fuming sulfuric acid, pyrosulfuric acid, chlorosulfonic acid,[3] sulfur trioxide,[4] $ClSO_3Si(CH_3)$,[5] $FSO_3.SbF_5$[6] and concentrated sulfuric acid *etc*. There are some disadvantages in these methods, for example the reaction time is long, the pollution is serious and some of the sulfonating agents are expensive.

In 1986 microwave irradiation was first adopted in organic synthesis,[7] and it has been used more and more in organic reactions since then. The sulfonation reactions of aromatic amines under microwave irradiation has not been reported. Here we first perform the sulfonation reaction of aromatic amines with 30~40% sulfuric acid as sulfonating agent under microwave irradiation (M.W.). We have obtained the corresponding amino aromatic sulfonic acids. Comparing with the classical methods, our programme is an efficient and simple one.



1(a-f) **2(a-f)**

Scheme 1

Table1 The sulfonation of aromatic amines with sulfuric acid

Entry	R_1	R_2	Reaction time/min MW/classical[a]	Yields/% MW/classical[a]
2a	H	H	4/300	93/87
2b	Me	H	2.5/120	84/68.6
2c	H	Me	3.5/1800	82/79
2d	Cl	H	3	87
2e	Br	H	2.5	78
2f	H	MeO	2	74

[a]The sulfonation of aromatic amines with concentrated sulfuric acid under the conditions of refluxing and stirring[3]

Experimental

The starting materials are chemically pure reagents. IR spectra were measured on a Bio-Rad FTS-40-spectrometer (KBr); ^1H NMR spectra were recorded on an AVANCE 400 spectrometer (DMSO), and the chemical shift was reported with TMS as an internal standard. MS were obtained on a VG 7070E spectrometer (FAB). Elemental analysis was determined using a Heraeus (CHN-O-RAPID) elemental analyser. The reactions were carried out in a SHARP-WP850A microwave oven.

General procedure

10 mmol aromatic amines were put into the Erlenmeyer flask where 40% sulfuric acid was added. The mixture was irradiated with the microwave oven at 70% output power for 2—4 minutes. After cooling down to room temperature, the mixture was neutralised to H=9—10 by saturated sodium carbonate solution. If necessary, the mixture was heated in order to accelerate dissolving. The mixture was extracted with diethyl ether, and the water-phase was adjusted to H=2 with 10% hydrochloric acid. Then the products would precipitate. The solution was thickened if the products did not crystallise. The results are summarised in Table 1.

DTA, IR, ^1H NMR, MS and elemental analysis data of the products:

4-aminobenzenesulfonic acid (**2a**)$^-$: DTA: 288°C (280–300°C);[9] IR (KBr): 3481 cm^{-1}, 1185 cm^{-1}, 1040 cm^{-1}, 830 cm^{-1}. ^1H NMR (DMSO, δ): 7.405–7.385 (2H, d, *J*=8Hz, 2-H and 6-H in $C_6\mathbf{H}_4$), 6.730–6.710(2H, d, *J*=8Hz, 3-H and 5-H in $C_6\mathbf{H}_4$)ppm. MS (*m*/*e*):173(M^+), 174. Elemental analysis: Found (%): C, 41.7; H, 4.03; N, 8.22; Calcd. For $C_6H_7NO_3S$ (%): C, 41.6; H, 4.04; N, 8.1

2-amino-5-methylbenzenesulfonic acid (**2b**): DTA:286–323°C (>30°C, decomposition);[8] IR (KBr): 3480 cm^{-1}, 3150 cm^{-1}, 1580 cm^{-1}, 1480 cm^{-1}, 815 cm^{-1}; ^1H NMR (DMSO, δ): 7.32 (1H, s, 6-H in $C_6\mathbf{H}_3$), 7.16–7.13 (1H, m, 4-H in $C_6\mathbf{H}_3$), 6.90–6.88 (1H, d, *J*=8Hz, 3-H in $C_6\mathbf{H}_3$)ppm. MS (*m*/*e*):187(M^+), 188 elemental analysis: Found (%): C, 44.8; H, 4.74; N, 7.61. Calcd. For $C_7H_9NO_3S$ (%): C, 44.9; H, 4.8; N, 7.5.

4-amino-3-methylbenzenesulfonic acid (**2c**): DTA: 135°C (132°C, decomposition);[9] IR (KBr): 3485 cm^{-1}, 2610 cm^{-1}, 1510 cm^{-1}, 1020 cm^{-1}, 810 cm^{-1}; ^1H NMR (DMSO, δ): 7.46–7.44 (1H, d, *J*=8Hz, 6-H in $C_6\mathbf{H}_3$), 7.42(1H, s, 2-H in $C_6\mathbf{H}_3$), 7.14–7.12 (1H, d, *J*=8Hz, 5-H in $C_6\mathbf{H}_3$), 2.25 (3H, s, $C\mathbf{H}_3$)ppm. MS (*m*/*e*):187(M^+), 188 Elemental analysis: Found (%): C, 44.8; H, 4.9; N, 7.34. Calcd. For $C_7H_9NO_3S$ (%): C, 44.9; H, 4.8; N, 7.5

2-amino-5-chloro-benzenesulfonic acid (**2d**): DTA: 282°C (>280°C, decomposition);[9] IR (KBr): 3480 cm^{-1}, 3150 cm^{-1}, 1580 cm^{-1}, 1480 cm^{-1}, 815 cm^{-1}; ^1H NMR (DMSO, δ): 7.52(1H, s, 6-H in $C_6\mathbf{H}_3$), 7.26–7.23 (1H, m, 4-H in $C_6\mathbf{H}_3$), 6.93–6.91 (1H, d, *J*=8Hz, 3-H in $C_6\mathbf{H}_3$)ppm. MS (*m*/*e*):206((M^+), 207; Elemental analysis: Found (%): C, 34.9; H, 2.84; N, 6.72 Calcd. For $C_6H_6NO_3ClS$ (%): C, 34.7; H, 2.9; N, 6.75

2-amino-5-bromo-benzenesulfonic acid (**2e**): DTA: 221°C, (decomposition); IR (KBr): 3480 cm^{-1}, 2620 cm^{-1}, 1190 cm^{-1}, 1045 cm^{-1}, 820 cm^{-1}; ^1H NMR (DMSO, δ): 7.69(1H, s, 6-H in $C_6\mathbf{H}_3$), 7.46–7.44 (1H, m, 4-H in $C_6\mathbf{H}_3$), 6.99–6.97 (1H, d, *J*=8Hz, 3-H in C_6H_3)ppm. MS (*m*/*e*):252(M+), 254. Elemental analysis: Found (%): C, 28.4; H, 2.41; N, 5.51; Calcd. For $C_6H_6NO_3SBr$ (%): C, 28.57; H, 2.38; N, 5.56.

4-amino-3-methyloxybenzenesulfonic acid (**2f**): DTA:263°C, (decomposition); IR (KBr): 3470 cm^{-1}, 2620 cm^{-1}, 1180 cm^{-1}, 1040 cm^{-1}, 860 cm^{-1}; ^1H NMR (DMSO, δ): 7.30–7.28(1H, d, J=8Hz, 6-H in $C_6\mathbf{H}_3$), 7.27(1H, s, 2-H in $C_6\mathbf{H}_3$), 7.24–7.22 (1H, d, *J*=8Hz, 5-H in $C_6\mathbf{H}_3$), 3.88 (s, 3H, $OC\mathbf{H}_3$)ppm. MS (*m*/*e*): 203(M+), 204. Elemental analysis: Found (%): C, 41.3; H, 4.40; N, 6.9. Calcd. For $C_6H_9NO_4S$ (%): C, 41.4; H, 4.43; N, 6.9.

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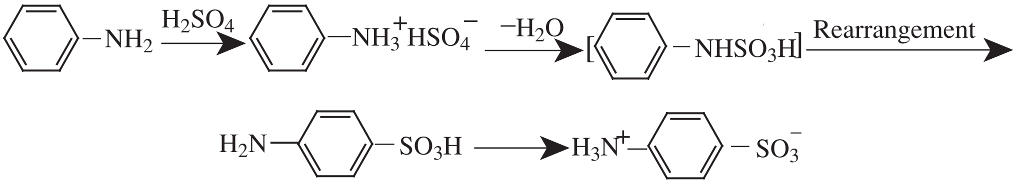
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.



Discussion

The process of reaction was monitored by thin layer chromatography. The products are inner salts, so the melting point (or decomposition temperature) is high, which has been measured through differential thermal analysis.

The heating under microwave is an internal one. Its character is rapid heating, with no terraced temperature and no hysteretic effect. Chemical reactions are accelerated under microwave irradiation because of selective absorption of microwave energy by polar molecules, at the start of the reaction, neutralisations between sulfuric acid and the aromatic amine occurs. Being strongly polar substances, the sulfates can be heated to high temperature in a few minutes. In such condition the products are obtained through dehydration and rearrangement of the sulfates. The following is the proposed mechanism for the sulfonation of aniline.

Because of the oxidising property of concentrated sulfuric acid, the amines oxidised easily, or even carbonised. So we selected the sulfuric acid with the concentration of 40% through experiment. The amount of the sulfuric acid should be in an excess to perfect the reaction, but too much acid would induce oxidation or carbonisation. The mole ratio of amine and acid selected through experiment is 1:1.1~1:1.3. 4-methylaniline and 4-nitroaniline are adopted in our experiment, but we can not get the expected products, it maybe the *meta* substituted group decrease the reactivity of the aromatic rings.

The peak of the amino group in ^{1}HNMR is broad in an acid environment and the range of chemical shift (δ) is 3.5-5. Because the melting point (or decomposition temperature) is high, MS are measured using FAB. Only the molecular ion-peak or M+1 peak can be observed clearly; the fragment peak abundance ratio is less.

Due to the absence of organic solvent and the selection of diluted sulfuric acid as sulfonating agent, we can alleviate the corruption of equipment; simplify the operation and save cost. In conclusion, we have found an ideal way to bring about the sulfonation of aromatic amines.

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