Polish J. Chem., **75**, 895–897 (2001) **COMMUNICATION**

Synthesis of New Sulfenic Acid Anilides from Aromatic Disulphides in the Presence of Silver Nitrate

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(Received November 16th, 2000; revised manuscript January 11th, 2001)

Compounds containing the sulphur-nitrogen bonds are of considerable importance, both from practical as well as theoretical standpoints. Sulfenic acid anilides are important intermediates in organic synthesis, which have been extensively used as sulphenyl-transfer reagents in the synthesis of sulphides [1], disulphides [2], trisulphides [3], sulphenate esters [4] and sulphenamides [5]. In the synthesis of sulfenic acid anilides, sulphenyl chlorides [6], thiols [7], sulphonyl acid derivatives [8] are used. Sulphenyl chlorides are thermally unstable and react easily with OH groups, active methylene groups and multiple bonds. Sulfenic acid anilides, containing these functional groups, cannot be prepared from the sulphenyl chloride. An important alternative method of sulfenic acid anilides synthesis is the metal-assisted reaction of disulphides and aromatic amines [9].

In this article we describe a one-step synthesis of sulfenic acid anilides from the aromatic disulphides and aniline or 4-aminothiophenol in the presence of silver nitrate in methanol (Scheme 1).

The present reaction is initiated by formation of a complex between Ag^+ and non-bonding electron pair on one sulphur atom of the R–S–S–R system, followed by nucleophilic displacement on the adjacent sulphur atom by amine group. Condensation of disulphides and thiols or amines afforded the new sulfenic acid anilides **6**–**8** with 34–45% yield. Then we have used a new sulfenic acid anilides **6**–**8** in the synthesis of polymers containing sulphenamide groups (-S-NH-) between phenyl rings.

General synthesis of sulfenic acid anilides: To 0.82 g (4.8 mmol) of silver nitrate dissolved in 75 ml of methanol, an equivalent amount of disulphide (**1**,**2**) was added and the reaction mixture was cooled in an ice bath. Then 2 equivalents of the appropriate amine (**3**) or thiol (**4**) were added and the reaction mixture was stirred for 3 h. The silver mercaptide (**9**,**10**) was filtrated and the filtrate evaporated under reduced pressure at 40°C. The resulting residue was dissolved in ether, washed with wa-

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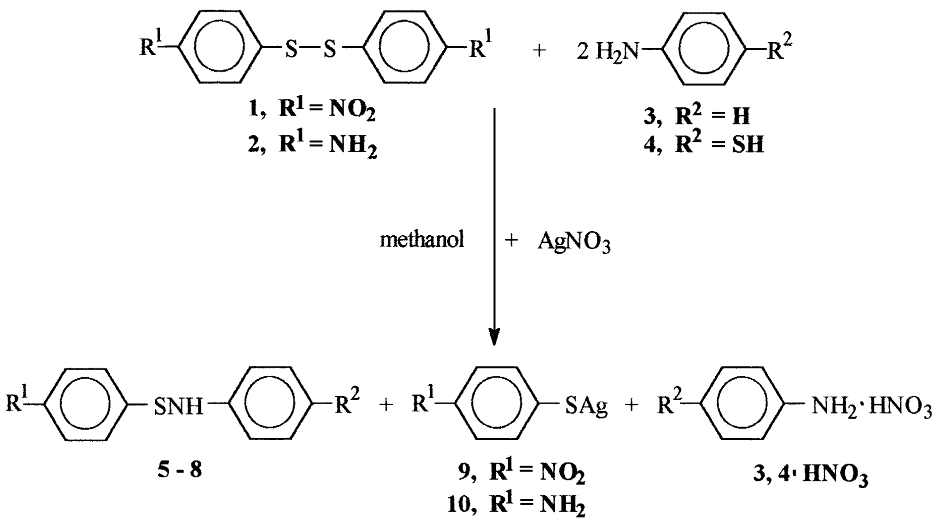
Scheme 1



	5	6	7	8
R^1	NO_2	NO_2	NH_2	NH_2
R^2	H	SH	H	SH

ter (100 ml), and dried over $MgSO_4$. Removal of the ethyl ether solvent gave the sulfenic acid anilides, which was distilled or crystallized. The following compounds were obtained:

4-Nitrobenzenesulfenic acid anilide (5): yellow crystals (40% yield): m.p. 69–70 °C(lit. [6] m.p. 68–70°C). IR (KBr, cm^{-1}): 3364 (-NH-), 1509 and 1330 ($-NO_2$), 837 (1,4-aromatic substitution), 750 (-S-NH-). ^1H NMR ($CDCl_3$, δ ppm): 5.25 (s, 1H, -NH-), 7.02–6.91 (m, 2H, aromatic), 7.33–7.22 (m, 2H, aromatic), 7.65–7.59 (m, 2H, aromatic), 8.23–8.10 (m, 3H, aromatic). ^{13}C NMR ($CDCl_3$, δ ppm): 114.65, 121.39, 121.71, 124.10, 124.41, 124.59, 126.39, 129.51, 131.10, 144.03, 145.39, 151.65. Anal. Calcd. for $C_{12}H_{10}N_2O_2S$: C, 58.54; H, 4.06; N, 11.38; S, 13.01. Found: C, 57.85; H, 3.92; N, 11.09; S, 12.77.

4-Nitrobenzenesulfenic acid 4′-mercaptoanilide (6): yellow crystals (34% yield): m.p. 155–156°C. IR (KBr, cm^{-1}): 3350 (-NH-), 2600 (-SH), 1516 and 1341 ($-NO_2$), 810 (1,4-aromatic substitution), 740 (-S-NH-). ^1H NMR (DMSO-d_6, δ ppm): 3. 52 (s, 1H, -SH), 7.27–7.24 (m, 4H, aromatic), 7.61–7.58 (m, 4H, aromatic), 8.23 (s, 1H, -NH-). ^{13}C NMR (DMSO-d_6, δ ppm): 122.32, 122.89, 124.38, 124.58, 126.66, 126.98, 129.79, 130.55, 133.31, 134.62, 145.14, 146.43. Anal. Calcd. for $C_{12}H_{10}N_2O_2S_2$: C, 51.80; H, 3.60; N, 10.07; S, 23.02. Found: C, 51.60; H, 3.30; N, 10.32; S, 23.40.

4-Aminobenzenesulphenic acid anilide (7): yellow thick oil (42% yield). IR (KBr, cm^{-1}): 3420 and 3350 (-NH$_2$), 3230 (-NH-), 810 (1,4-aromatic substitution), 740 (-S-NH-). ^{1}H NMR (DMSO-d$_6$, δ ppm): 7.52–7.48 (d, 2H, -NH-), 7.39–7.32 (d, 2H, -NH$_2$), 7.01–6.95 (m, 4H, aromatic), 7.24–7.18 (m, 5H, aromatic). ^{13}C NMR (DMSO-d$_6$, δ ppm): 114.95, 119.33, 119.57, 122.06, 122.12, 124,27, 126.93, 127.07, 127.15, 129.34, 131.33, 138.46. Anal. Calcd. for $C_{12}H_{12}N_2S$: C, 66.67; H, 5.56; N, 12.96; S, 14.81. Found: C, 65.97; H, 5.40; N, 11.79; S, 14.11.

4-Aminobenzenesulfenic acid 4′-mercaptoanilide (8): yellow thick oil (45% yield). IR (KBr, cm^{-1}): 3450 and 3380 (-NH$_2$), 3210 (-NH-), 2600 (-SH), 840 (1,4-aromatic substitution), 750 (-S-NH-). ^{1}H NMR (DMSO-d$_6$, δ ppm): 3.55 (s, 1H, -SH), 6.68–6.65 (d, 1H, -NH-), 7.18–7.16 (d, 2H, -NH$_2$), 7.26–7.23 (m, 4H, aromatic), 6.74–6.71 (m, 4H, aromatic). ^{13}C NMR (DMSO-d$_6$, δ ppm): 115.37, 115.69, 116.10, 116.44, 118.56, 118.69, 123.54, 131.07, 131.89, 133.27, 133.77, 146.49. Anal. Calcd. for $C_{12}H_{12}N_2S_2$: C, 58.06; H, 4.84; N, 11.29; S, 25.81. Found: C, 59.95; H, 4.71; N, 11.01; S, 25.27.

Acknowledgment

This work was supported by the University grant DS 32/11/2000.

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