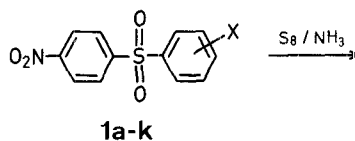


of the 4-nitroaniline (**3**) and the 4,4'-dinitrodiphenyl disulfide (**4**) from 4-chloronitrobenzene and elemental sulfur in liquid ammonia⁶.



Reactions of 4-Nitrophenyl-Substituted-Phenyl-Sulfones with Elemental Sulfur in Liquid Ammonia: One-Pot Synthesis of Ammonium Arenethiosulfonates from Aromatic Nitro Sulfones

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Thiosulfonic acids, thioacids of sulfonic acids, which are believed to have anti-tumour and anti-enzyme properties¹ are also important intermediates for synthesis of thiol-sulfonates². However, there have been only a few reports on the preparation of thiosulfonic acids^{3,4}. Recently, we reported that the reactions of sodium arenesulfonates with elemental sulfur in liquid ammonia or various amines afford sodium arenethiosulfonates at room temperature quantitatively⁵. It is still, however, difficult to introduce various substituents into the benzene rings of the arenethiosulfonates by these methods.

We have now found that the aromatic nitro sulfones **1** react with elemental sulfur in liquid ammonia to give the corresponding ammonium arenethiosulfonates **2** in good yields in addition to other products such as 4-nitroaniline (**3**) and 4,4'-dinitrodiphenyl disulfide (**4**). We have previously reported on the formation

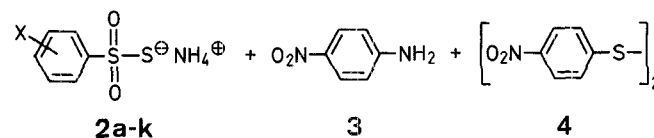


Table 1. Reactions of Sulfones **1a-k** with Elemental Sulfur in Liquid Ammonia

Substrate No.	Reaction temp. [°C]	Reaction time [h]	Amount of S ₈ (mg-atom)	Yield [%] ^a of		
				2	3	4
1a	4-H ₃ CO	60°	2	1	39	3
1a		100°	2	1	69	14
1a		60°	2	2	70	4
1a		100°	2	2	84	35
1a		100°	2	3	100	32
1b	4-Cl	100°	2	2	74	43
1c	H	100°	2	2	65	12
1d	4-H ₂ N	100°	2	2	59	—
1e	4-O ₂ N	40°	2	2	98	—
1f	3-C ₂ H ₅ O	100°	2	2	94	40
1g	3-H ₃ CO	100°	2	2	90	33
1h	3-H ₃ C	100°	2	2	100	40
1i	3,5-di-Cl	100°	2	2	93	40
1j	2-H ₃ CO	100°	2	2	67	23
1k	2-H ₃ C	100°	2	2	79	18

^a Yield of crude products based on **1** employed.

^b 4,4'-Dinitrodiphenyl sulfide was also obtained.

Table 2. Ammonium Arenethiosulfonate **2a-k**

Prod-uct	m.p. [°C]	Molecular formula ^a	I.R. (KBr) ν [cm ⁻¹]	¹ H-N.M.R. (DMSO- <i>d</i> ₆) δ [ppm]
2a	94° (dec.)	C ₇ H ₁₁ NO ₃ S ₂ (221.3)	3170, 1430 (NH ₄ ⁺), 1150 (SO ₂)	7.68 (d, 2H, <i>J</i> = 8.4 Hz); 6.89 (d, 2H, <i>J</i> = 8.4 Hz); 7.12 (s, 4H); 3.77 (s, 3H)
2b	149°	C ₆ H ₈ ClNO ₂ S ₂ (225.7)	3200, 1410 (NH ₄ ⁺), 1170 (SO ₂)	7.76 (d, 2H, <i>J</i> = 8.0 Hz); 7.41 (d, 2H, <i>J</i> = 8.0 Hz); 7.12 (s, 4H)
2c	116°	C ₆ H ₉ NO ₂ S ₂ (191.3)	3100, 1400 (NH ₄ ⁺), 1180 (SO ₂)	7.84–7.29 (m, 5H); 7.10 (s, 4H)
2d	183° (dec.)	C ₆ H ₁₀ N ₂ O ₂ S ₂ (206.3)	3200, 1400 (NH ₄ ⁺), 1260 (SO ₂)	7.40 (d, 2H, <i>J</i> = 8.0 Hz); 6.46 (d, 2H, <i>J</i> = 8.0 Hz); 7.12 (s, 4H); 5.31 (s, 2H)
2e	187° (dec.)	C ₆ H ₈ N ₂ O ₄ S ₂ (236.3)	3180, 1400 (NH ₄ ⁺), 1520, 1350 (NO ₂)	8.25 (d, 2H, <i>J</i> = 8.4 Hz); 7.96 (d, 2H, <i>J</i> = 8.4 Hz); 7.12 (s, 4H)
2f	120°	C ₈ H ₁₃ NO ₃ S ₂ (235.3)	3150, 1400 (NH ₄ ⁺), 3000, 2940 (C ₂ H ₅)	7.33–6.78 (m, 4H); 7.08 (s, 4H); 4.01 (q, 2H, <i>J</i> = 3.5 Hz); 1.30 (t, 3H, <i>J</i> = 3.5 Hz)
2g	197° (dec.)	C ₇ H ₁₁ NO ₃ S ₂ (221.3)	3150, 1400 (NH ₄ ⁺), 3000 (CH ₃)	7.33–6.80 (m, 4H); 7.07 (s, 4H); 3.72 (s, 3H)
2h	150°	C ₇ H ₁₁ NO ₂ S ₂ (205.3)	3170, 1400 (NH ₄ ⁺), 1190 (SO ₂)	7.62–6.80 (m, 4H); 7.10 (NH ₄ ⁺); 2.30 (s, 3H)
2i	185° (dec.)	C ₆ H ₇ Cl ₂ NO ₂ S ₂ (260.2)	3150, 1400 (NH ₄ ⁺), 1180 (SO ₂)	7.69–7.54 (m, 3H); 7.06 (s, 4H)
2j	197° (dec.)	C ₇ H ₁₁ NO ₃ S ₂ (221.3)	3170, 1420 (NH ₄ ⁺), 2850 (CH ₃)	7.87–6.75 (m, 4H); 7.12 (s, 4H); 3.78 (s, 3H)
2k	145°	C ₇ H ₁₁ NO ₂ S ₂ (205.3)	3160, 1400 (NH ₄ ⁺), 1170 (SO ₂)	7.87–6.95 (m, 4H); 7.11 (s, 4H); 2.66 (s, 3H)

^a Satisfactory microanalyses obtained: C \pm 0.29, H \pm 0.23, N \pm 0.32).

Thus, various ammonium arenethiosulfonates **2** were obtained in good yield by the reactions of sulfones **1** with elemental sulfur in liquid ammonia without the necessity of using arenesulfinates or arenesulfonyl chlorides as starting materials.

The 4-nitrophenyl-substituted-phenyl-sulfones **1a-k** were prepared from the corresponding sulfides according to Ref.⁷

Ammonium Arenethiosulfonates **2; General Procedure:**

A mixture of the aromatic nitro sulfone **1** (1 mmol) and elemental sulfur (1–3 mg atom) in liquid ammonia (10 ml) is allowed to react with stirring at 40–100 °C in a titanium autoclave as reaction vessel. The ammonia in the reaction mixture is removed by evaporation, and then the residue is extracted with anhydrous chloroform (10 ml) after extraction with anhydrous ether (~10 ml). The solutions of ether and of chloroform contain 4-nitroaniline (**3**) and 4,4'-dinitrodiphenyl disulfide (**4**), respectively. Ammonium arenethiosulfonate **2** is obtained by extraction of the insoluble material with methanol (~10 ml). The ammonium arenethiosulfonate **2** is recrystallized from methanol/hexane. The reaction can also be carried out a 500 mmol or larger scale.

Received: August 18, 1980

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