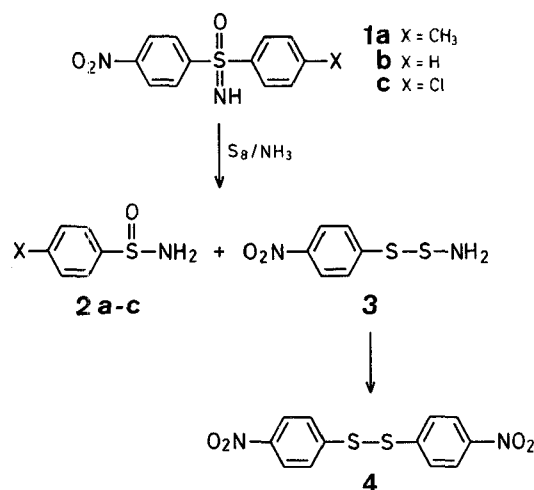
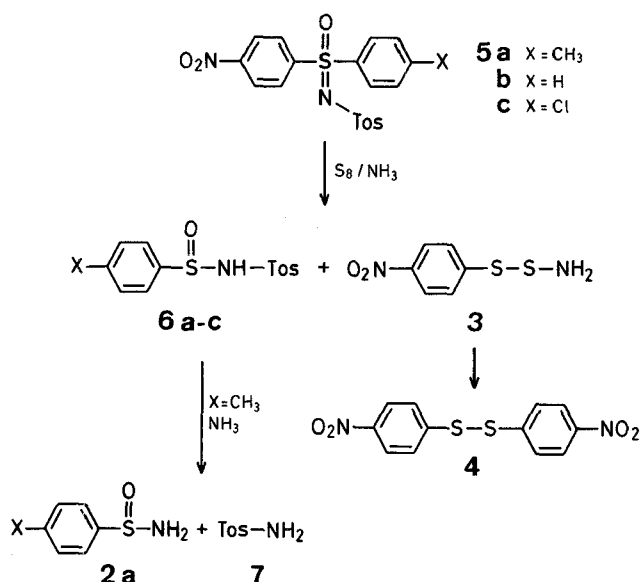




Scheme A

In the case of *N*-tosyl derivatives, e.g. **5a**, the resulting sulfinamide, e.g. **6a**, further reacts with nucleophiles such as ammonia or aminothiols yielding 4-methylbenzenesulfinamide (**2a**) and 4-methylbenzenesulfonamide (**7**) (Scheme B and Tables).



Scheme B

Since the arenesulfinamides have been found to be reduced by elemental sulfur in liquid ammonia to give diaryl disulfides, the yields of the arenesulfinamides in runs 3 and 7 in Table 1 are relatively low. The obtained products were identified by ¹H-N.M.R., I.R., and microanalytical data (Table 2).

Table 1. Arenesulfinamides **2** and **6** from *S*-4-Nitrophenyl *S*-Substituted-Phenyl Sulfoximides **1** and **5**

Run	Substrate	Amount of sulfur (mmol)	Reaction temperature	Product	Yield ^a [%]
1	5a	1	20°C	6a	100
2	5a	1	80°C	6a + 2a	40 + 41
3	1a	2	60°C	2a	81
4	5b	1	40°C	6b	100
5	1b	2	60°C	2b	90
6	5c	1	40°C	6c	100
7	1c	2	60°C	2c	68

^a Yield of isolated product.

A Novel Synthesis of Arenesulfinamides from *S*-4-Nitrophenyl *S*-Substituted-Phenyl Sulfoximides with Elemental Sulfur in Liquid Ammonia

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The numerous reported methods on the preparation of arenesulfinamides are very complex and limited regarding the yields¹. Much work has been centered on improving the yields of the arenesulfinamides^{2,3,4} but there is still a need for a better method. We have already reported some reactions of organosulfur compounds and others with elemental sulfur in liquid ammonia and revealed the reactivity of elemental sulfur in liquid ammonia^{4,5}.

We have now found a new method to prepare arenesulfinamides in excellent yields from *S*-4-nitrophenyl *S*-substituted-phenyl sulfoximides **1** with elemental sulfur in liquid ammonia. In these reactions also, ammonium aminothiols (H₂NS⁺NH₄⁺) or aminodithiols (H₂NSS⁺NH₄⁺), which are formed from elemental sulfur in liquid ammonia⁶, attacks the 1-arylcarbon of the 4-nitrophenyl ring of the substrate affording the desired arenesulfinamides **2** and 4-nitrobenzenethiosulfenamide (**3**). The thiosulfenamide **3** has been found to react further with elemental sulfur in liquid ammonia giving 4,4'-dinitrodiphenyl disulfide (**4**)⁶ (Scheme A).

Table 2. Physical Data for Products 2a-c and 6a-c

Prod- uct	m.p. [°C]	Molecular formula ^a or Lit. m.p. [°C]	I.R. (KBr) ν [cm ⁻¹]	¹ H-N.M.R. (CDCl ₃ /TMS) δ [ppm]
2a	115°	C ₇ H ₉ NOS (155.2)	3700 (NH ₂); 1080 (S=O); 1480 (CH ₃)	2.37 (s, 3 H, CH ₃); 4.44 (s, 2 H, NH ₂); 7.25 (d, $J=9.0$ Hz, 2 H _{arom}); 7.59 (d, $J=9.0$ Hz, 2 H _{arom})
2b	121°	C ₆ H ₇ NOS (141.2)	3690 (NH ₂); 1075 (S=O)	4.48 (s, 2 H, NH ₂); 7.4-7.5 (m, 3 H _{arom}); 7.7-7.8 (m, 2 H _{arom})
2c	135°	C ₆ H ₈ ClNOS (175.6)	3650 (NH ₂); 1080 (S=O)	4.44 (s, 2 H, NH ₂); 7.46 (d, $J=9.0$ Hz, 2 H _{arom}); 7.66 (d, $J=9.0$ Hz, 2 H _{arom})
6a	123° (dec)	C ₁₄ H ₁₅ NO ₃ S ₂ (309.4)	3300 (NH); 2980 (CH ₃); 1360, 1145 (SO ₂); 1060 (S=O)	2.21 (s, 3 H, CH ₃); 2.26 (s, 3 H, CH ₃); 6.64 (br. s, 1 H, NH); 6.97 (d, $J=8.0$ Hz, 2 H _{arom}); 7.03 (d, $J=8.0$ Hz, 2 H _{arom}); 7.23 (d, $J=8.0$ Hz, 2 H _{arom}); 7.66 (d, $J=8.0$ Hz, 2 H _{arom})
6b	126° (dec)	C ₁₃ H ₁₃ NO ₃ S ₂ (295.4)	3400 (NH); 2950 (CH ₃); 1380, 1140 (SO ₂); 1070 (S=O)	2.24 (s, 3 H, CH ₃); 6.97 (d, $J=8.0$ Hz, 2 H _{arom}); 7.0-7.5 (m, 4 H _{arom}); 7.63 (d, $J=8.0$ Hz, 2 H _{arom})
6c	138° (dec)	C ₁₃ H ₁₂ ClNO ₃ S ₂ (329.8)	3450 (NH); 2980 (CH ₃); 1390, 1150 (SO ₂); 1085 (S=O)	2.28 (s, 3 H, CH ₃); 6.71 (br. s, 1 H, NH); 6.8-7.0 (m, 4 H _{arom}); 7.19 (d, $J=8.0$ Hz, 2 H _{arom}); 7.59 (d, $J=8.0$ Hz, 2 H _{arom})

^a Satisfactory microanalyses obtained: C ± 0.41 , H ± 0.34 , N ± 0.36 .

The *S*-4-nitrophenyl *S*-substituted-phenyl sulfoximides 1a-c and 5a-c are prepared according to Ref.⁷.

Arenesulfonamides 2 and 6 from *S*-4-Nitrophenyl *S*-Substituted Phenyl Sulfoximides 1 and 5; General Procedure:

A titanium autoclave filled with compound 1 or 5 (1 mmol) and elemental sulfur (1 or 2 mmol) is evacuated and liquid ammonia (10 ml) is added. The autoclave is heated at the temperature given in Table 1 for 3 h, cooled, and opened. The reaction mixture is chromatographed over silica gel (Wako gel C-300) using chloroform/ether (3:1) as eluent to give the product 2 or 6 (Tables 1 and 2).

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- ¹ L. C. Raiford, S. E. Hazlet, *J. Am. Chem. Soc.* **57**, 2172 (1935).
- I. B. Douglass, B. S. Farsh, *J. Org. Chem.* **23**, 805 (1958).
- J. Jaconbus, K. Mislow, *J. Chem. Soc. Chem. Commun.* **1969**, 253.
- H. Gilmann, H. L. Marris, *J. Am. Chem. Soc.* **48**, 2399 (1926).
- D. Klamann, C. San, M. Zelenka, *Chem. Ber.* **92**, 1910 (1959).
- ² D. N. Harpp, T. G. Back, *Tetrahedron Lett.* **1972**, 5313.
- D. N. Harpp, T. G. Back, *J. Org. Chem.* **38**, 4323 (1973).
- M. Furukawa, T. Ohkawara, *Synthesis* **1976**, 339.
- M. Furukawa, T. Ohkawara, Y. Noguchi, *Chem. Pharm. Bull.* **1980**, 134.
- ³ M. Haake, H. Gebbing, H. Benack, *Synthesis* **1979**, 97.
- ⁴ R. Sato, S. Chiba, Y. Takikawa, S. Takizawa, M. Saito, *Chem. Lett.* **1983**, 535.
- ⁵ R. Sato, T. Goto, Y. Takikawa, S. Takizawa, *Synthesis* **1980**, 615.
- R. Sato, T. Etchu, Y. Takikawa, S. Takizawa, M. Saito, *Synthesis* **1981**, 44.
- ⁶ R. Sato, K. Araya, Y. Takikawa, S. Takizawa, S. Oae, *Phosphorus Sulfur* **5**, 245 (1978).
- R. Sato, T. Sato, K. Segawa, Y. Takikawa, S. Takizawa, S. Oae, *Phosphorus Sulfur* **7**, 217 (1979).
- ⁷ N. Furukawa, K. Akutagawa, T. Yoshimura, S. Oae, *Tetrahedron Lett.* **22**, 3089 (1981).