



Table 1. Reactions of 4-Nitrophenyl Substituted Phenyl Sulfoxides,  $O_2N-C_6H_4-SO-C_6H_4-X$ , with Elemental Sulfur in Liquid Ammonia<sup>a)</sup>

Run	Substituent X		React		S <sub>8</sub> (mg atom)	Yield of Sulfinamides(%) X-C <sub>6</sub> H <sub>4</sub> -SONH <sub>2</sub>
			Temp (°C)	Time(h)		
1	CH <sub>3</sub>	1a	20	2	2	65
2	CH <sub>3</sub>	1a	20	6	2	66
3	CH <sub>3</sub>	1a	60	2	2	49
4	CH <sub>3</sub>	1a	80	2	2	8
5	CH <sub>3</sub>	1a	20	2	1	43
6	CH <sub>3</sub>	1a	20	2	3	57
7	Cl	1b	20	6	2	65
8	H	1c	60	2	2	58
9	NO <sub>2</sub>	1d	20	2	2	38
10 <sup>b)</sup>	CH <sub>3</sub>	1a	20	2	0	trace

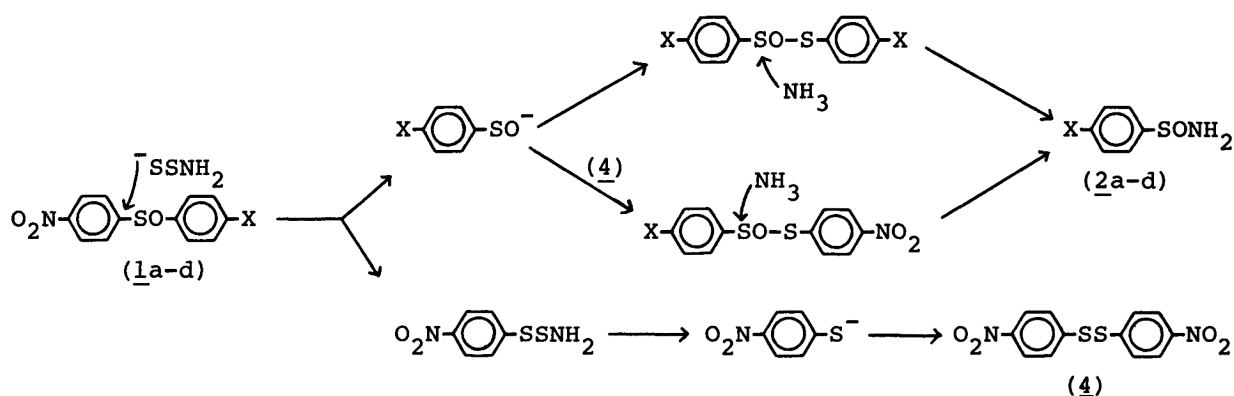
a) Substrate: 1 mmol, Liquid Ammonia: 10 ml,

b) Benzenethiol (2 mmol) was added.

by the reactions of arenethiols with 4-chloronitrobenzene in liquid ammonia and subsequent oxidation with hydrogen peroxide in acetic acid. In this reaction, products are arenesulfinamides(2a-d), diaryl disulfides(3a-d) and 4,4'-dinitrodiphenyl disulfide(4). Typical procedure is as follows.

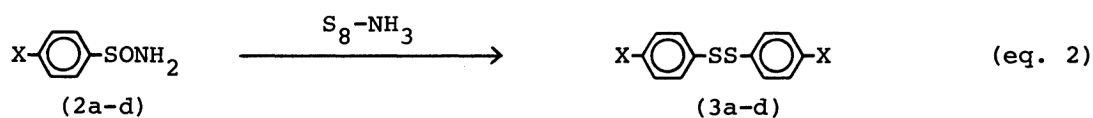
4-Nitrophenyl substituted phenyl sulfoxide and elemental sulfur were taken into all titanium autoclave. After evacuation liquid ammonia is charged into the autoclave. Reaction mixtures were separated by column chromatography on silica gel(Wako gel C-300) using chloroform as eluent. The obtained sulfinamides(2a-d) were identified by NMR, Mass, IR and elemental analysis. Results of this reaction are summarized in Table 1.

The results in Table 1 show that various arenesulfinamides are obtained in good yields by one-pot reactions of 4-nitrophenyl substituted phenyl sulfoxide with elemental sulfur in liquid ammonia at low temperature such as 20°C.(Run 2,7, 8 and 9) When benzenethiol instead of elemental sulfur was used in this reaction, desired sulfinamide was obtained only in trace(run 10). This fact suggests that the elemental sulfur in liquid ammonia plays an important role in this reaction. We have already reported the formation of ammonium aminothiolate or aminodithiolate,  $H_2NS^-NH_4^+$  or  $H_2NSS^-NH_4^+$ , and its nucleophilic reactions toward 4-chloronitrobenzene<sup>8)</sup> and benzylchloride<sup>9)</sup> to give sulfides. In the present reaction, aminothiolate apparently attacks on 1-arylcarbon of 4-nitrophenyl ring at initial stage to leave ammonium arenesulfenate. Recently we have reported the reactions of 4-nitrophenyl aryl and alkyl sulfones with elemental sulfur in liquid ammonia to yield aryl<sup>7)</sup> and alkyl<sup>10)</sup> thiosulfonic acids. These reactions were also illustrated by the initial attack of aminothiolate on 1-arylcarbon of 4-nitrophenyl ring. Sulfenic acid is well known to disproportionate to thiolsulfinate.<sup>11)</sup> The formation of arenesulfinamides can be interpreted by



the nucleophilic attack of ammonia on sulfinyl sulfur of the thiolate. However, since the high yields of the sulfinamides (run 2) cannot be explained by only above mechanism, another path is necessary to consider. Another path is an attack of arenesulfinate anion on sulfenyl sulfur in 4,4'-dinitrodiphenyl disulfide (4), which is formed from 4-nitrobenzenethiosulfenamide,  $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{SSNH}_2$ , with elemental sulfur in liquid ammonia,<sup>12)</sup> affording 4-nitrophenyl benzenethiolate,  $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{S}-\text{SO}-\text{C}_6\text{H}_4-\text{X}$ , and then nucleophilic attack of ammonia on sulfinyl sulfur of the thiolate giving arenesulfinamide and 4-nitrobenzene thiolate. These are depicted in Scheme 1.

Surprisingly, in the reactions at high temperature such as 80°C and 100°C the yield of arenesulfinamide decreased. The yields of sulfinamides were low in the cases of the reactions for long time and using 3 mg atom of elemental sulfur. These results suggest that the sulfinamides resulted further react with elemental sulfur in liquid ammonia (eq. 2). To confirm these reactions



we carried out the reactions of arenesulfinamides with elemental sulfur in liquid ammonia and found the reduction of arenesulfinamides to corresponding diaryl

Table 2. Reactions of Arenesulfinamides with Elemental Sulfur in Liquid Ammonia<sup>a)</sup>

Run	Sulfinamide $\text{X}-\text{C}_6\text{H}_4-\text{SONH}_2$	React. Temp (°C)	$\text{S}_8$ (mg atom)	Yield of product (%) $\text{X}-\text{C}_6\text{H}_4-\text{SS}-\text{C}_6\text{H}_4-\text{X}$
1	$\text{CH}_3-\text{C}_6\text{H}_4-\text{SONH}_2$	60	2	$\text{CH}_3-\text{C}_6\text{H}_4-\text{SS}-\text{C}_6\text{H}_4-\text{CH}_3$ 32
2		80	2	62
3		100	2	76
4		100	3	83
5		100	1	41
6	$\text{C}_6\text{H}_5-\text{SONH}_2$	100	3	$\text{C}_6\text{H}_5-\text{SS}-\text{C}_6\text{H}_5$ 89
7		100	2	79
8		100	1	44

a) Substrate: 1 mmol, Liquid Ammonia: 10 ml, Reaction Time: 4 h,

disulfides in good yields. These results are summarized in Table 2.

Thus the arenesulfinamides were reduced with elemental sulfur in liquid ammonia at high temperature such as 100°C affording diaryl disulfides (run 3, 4, and 6). Accordingly, the low yields of run 4 and 6 in Table 1 are interpreted by the reaction of arenesulfinamides with elemental sulfur in liquid ammonia. We have already reported the reduction with elemental sulfur in liquid ammonia, e.g. the reduction of nitrogen functional groups.<sup>13, 14)</sup> Above results suggest that the reaction system of elemental sulfur in liquid ammonia is very useful for the reduction of not only nitrogen functional groups but also sulfur functional groups.

Thus arenesulfinamides were synthesized in good yields and were further reduced to corresponding diaryl disulfides with elemental sulfur in liquid ammonia. These reactions are also very important as conversion of arenethiols to arenesulfinamides with elemental sulfur in liquid ammonia. The applications for synthetic chemistry of elemental sulfur in liquid ammonia are now in progress.

#### References

- 1) a) L. C. Raiford and S. E. Hazlet, *J. Am. Chem. Soc.*, **57**, 2172(1935).  
b) I. B. Douglass and B. S. Farsh, *J. Org. Chem.*, **23**, 805(1958).  
c) J. Jacombus and K. Mislow, *J. Chem. Soc., Chem. Commun.*, **1969**, 253.
- 2) a) H. Gilmann and H. L. Marris, *J. Am. Chem. Soc.*, **48**, 2399(1926).  
b) D. Klamann, C. San and M. Zelenka, *Chem. Ber.*, **92**, 1910(1959).
- 3) a) D. N. Harpp and T. G. Back, *Tetrahedron Lett.*, **1972**, 5313.  
b) D. N. Harpp and T. G. Back, *J. Org. Chem.*, **38**, 4323(1973).
- 4) a) M. Furukawa and T. Ohkawara, *Synthesis*, **1976**, 339.  
b) M. Furukawa, T. Ohkawara, and Y. Noguchi, *Chem. Pharm. Bull.*, **1980**, 134.
- 5) M. Haake, H. Gebbing, and H. Benack, *Synthesis*, **1979**, 97.
- 6) R. Sato, T. Goto, Y. Takikawa, and S. Takizawa, *Synthesis*, **1980**, 615.
- 7) R. Sato, T. Etchu, Y. Takikawa, S. Takizawa, and M. Saito, *Synthesis*, **1981**, 44.
- 8) R. Sato, T. Sato, K. Segawa, Y. Takikawa, S. Takizawa, and S. Oae, *Phosphorus and Sulfur*, **7**, 217(1979).
- 9) R. Sato, T. Goto, K. Kakuta, Y. Takikawa, S. Takizawa, and S. Oae, *Phosphorus and Sulfur*, **7**, 289(1979).
- 10) R. Sato, T. Etchu, M. Kato, M. Sato, and M. Saito, *Chem. Lett.*, in contribution.
- 11) "Yuki Iō Kagaku, Han-no Hen," ed by S. Oae, *Kagaku Dojin*, Kyoto(1982) pp.131-162.
- 12) R. Sato, K. Araya, Y. Takikawa, S. Takizawa, and S. Oae, *Phosphorus and Sulfur*, **5**, 245(1978).
- 13) R. Sato, S. Takizawa, and S. Oae, *Phosphorus and Sulfur*, **7**, 229(1979).
- 14) R. Sato, R. Kawasaki, H. Takahashi, S. Yamaichi, and M. Saito, *Phosphorus and Sulfur*, in contribution.

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