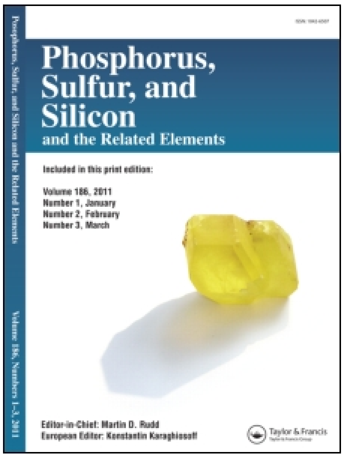

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REACTIONS OF 4-NITROPHENYLSUBSTITUTED PHENYL SULFIDES AND RELATED COMPOUNDS WITH ELEMENTAL SULFUR IN LIQUID AMMONIA: FORMATION OF UNSYMMETRICAL AROMATIC DISULFIDES

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REACTIONS OF 4-NITROPHENYL-SUBSTITUTED PHENYL SULFIDES AND RELATED COMPOUNDS WITH ELEMENTAL SULFUR IN LIQUID AMMONIA: FORMATION OF UNSYMMETRICAL AROMATIC DISULFIDES

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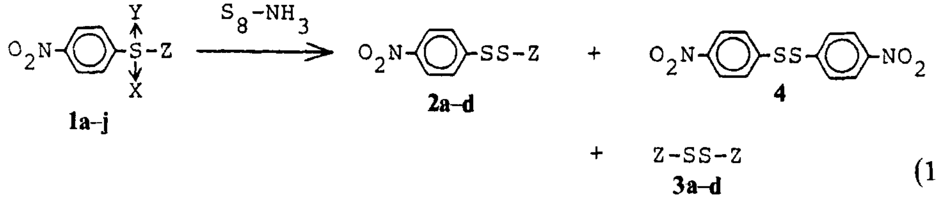
Various unsymmetrical disulfides in addition to symmetrical disulfides were obtained in moderate yields by the reactions of 4-nitrophenyl-substituted phenyl sulfides and related compounds such as *S*-4-nitrophenyl *S*-substituted phenyl sulfimides and sulfodiimides with elemental sulfur in the polar basic solvent, liquid ammonia. The mechanism of these reactions is discussed in the light of the role of elemental sulfur in liquid ammonia.

INTRODUCTION

The aliphatic and aromatic disulfides are very important compounds in organic synthetic chemistry and biological chemistry. In particular, much attention has been focused on the characterization and synthesis of unsymmetrical disulfides which are very significant in biochemistry.[1] For example, A. F. Beecham *et al.* reported the structure and absolute configurations of sporidesmin[2] and K. K. Andersen *et al.* characterized trans-2-butyl methyl disulfide as the malodorous volatile portion of the scent of the striped skunk.[3] There have been numerous reports on the preparations of unsymmetrical aliphatic disulfides,[4] e.g., (a) thiolations of sulfenyl halides and thiosulfonates and (b) alkylthiolations of Bunte salts, sulfenylthiocyanates, sulfenylthiocarbonates, thionitrites and others. Only a few methods for unsymmetrical aromatic disulfides have been reported, however, because of the lability of unsymmetrical aromatic disulfides to disproportionate to symmetrical disulfides.[5] During the course of our investigations on the reactions of organosulfur compounds with elemental sulfur in liquid ammonia and amines,[6] we explored a new synthetic method for unsymmetrical aromatic disulfides. We have now found a new route to unsymmetrical aromatic disulfides in addition to symmetrical aromatic disulfides from 4-nitrophenyl-substituted phenyl sulfides and related compounds such as *S*-4-nitrophenyl *S*-substituted phenyl sulfimides and sulfodiimides with elemental sulfur in liquid ammonia, a polar basic solvent, as follows (Eq. (1)):



(1)

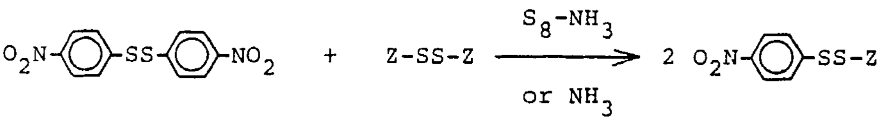
To our knowledge, there have been no reports on the direct formation of disulfides from monosulfides and related compounds such as sulfimides and sulfodiimides.

RESULTS AND DISCUSSION

As shown in Table I various unsymmetrical aromatic disulfides (**2a–d**) and symmetrical disulfides, 4,4′-dinitrodiphenyl disulfide (**4**) and 4,4′-disubstituted diphenyl disulfides (**3a–d**), were obtained by the reactions of 4-nitrophenyl-substituted phenyl sulfides (**1a–c**) and related compounds such as *S*-4-nitrophenyl *S*-substituted phenyl sulfimides (**1d–h**) and sulfodiimides (**1i–j**) with elemental sulfur in liquid ammonia. Particularly in the case of the reaction of *N*-tosyl *S*-4-nitrophenyl *S*-substituted phenyl sulfimide (**1d**), the unsymmetrical disulfide (**2a**) was obtained in maximum yield, 51% (run 6). Since the disproportionation of the unsymmetrical disulfides to symmetrical disulfides upon heating is well known,[7] it is noteworthy that the unsymmetrical disulfides are produced in reasonable yields even at high temperatures such as 100°C (runs 1 and 3).

These results are interpreted in the light of the role of elemental sulfur in liquid ammonia. We have already reported the formation of ammonium aminothiolate, $H_2NS^-NH_4^+$, or ammonium aminodithiolate, $H_2NSS^-NH_4^+$, from elemental sulfur in liquid ammonia[8] and the reactions of organosulfur compounds with the aminothiolates.[6] In the present reaction, the initial stage is apparently a nucleophilic attack of the aminothiolate ion on the 1-aryl carbon of the 4-nitrophenyl ring in the substrate to release 4-substituted benzenethiolate (runs 1–4) or benzenesulfenamides (runs 5–12). The resulting 4-nitrobenzenethiosulfenamide, benzenethiolate and benzenesulfenamides react further with elemental sulfur in liquid ammonia affording unsymmetrical aromatic disulfides accompanied by symmetrical aromatic disulfides as depicted in Scheme 1.[9]

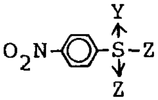
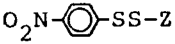
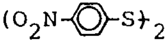
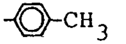
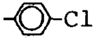
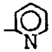
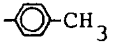
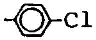
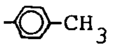
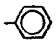
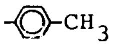
In addition, we examined the possibility of direct formation unsymmetrical aromatic disulfides from symmetrical aromatic disulfides in liquid ammonia, that is, a sulfide exchange reaction as shown in Eq. (2).



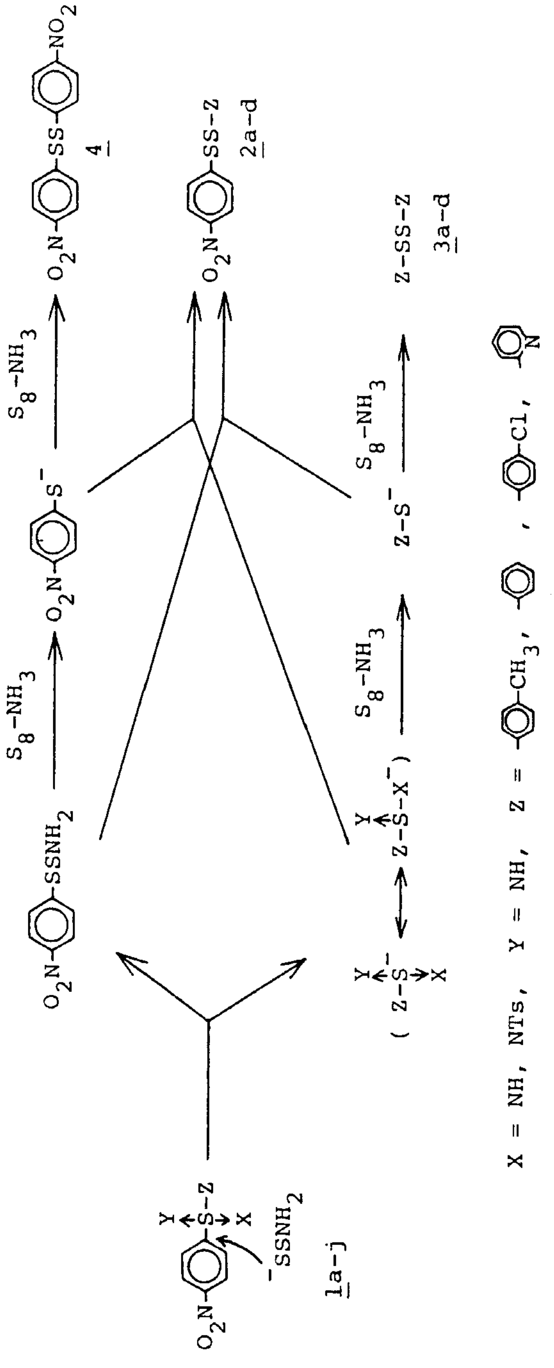
(2)

TABLE I

Reaction of 4-nitrophenyl substituted phenyl sulfides and related compounds with elemental sulfur in liquid ammonia

	Substrate: 				Reaction			Yield of disulfide/%[b]					
Run[a]	X	Y	Z		Tem/°C	Time/h	S_8/mg atom			Z—SS—Z			
1	—	—		**1a**	100	4	3	35	**2a**	29	**3a**	36	**4**
2	—	—	″	″	60	4	2	8	″	24	″	32	″
3	—	—		**1b**	100	2	3	35	**2b**	20	**3b**	45	**4**
4	—	—		**1c**	80	4	3	33	**2c**	31	**3c**	36	″
5	NTs	—		**1d**	60	2	2	44	**2a**	42	**3a**	14	″
6	″	—	″	″	40	2	4	51	″	46	″	3	″
7	″	—		**1e**	40	2	2	43[c]	**2d**	55	**3d**	2	″
8	NTs	—		**1f**	40	2	2	50[c]	**2b**	33	**3b**	17	″
9	NH	—		**1g**	40	2	4	46	**2a**	36	**3a**	18	″
10	″	—		**1h**	40	2	2	58[c]	**2d**	40	**3d**	2	″
11	NTs	NH		**1i**	60	3	4	40	**2a**	43	**3a**	17	″
12	NH	″	″	**1j**	60	2	4	27	″	61	″	12	″

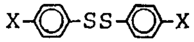
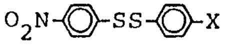
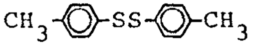
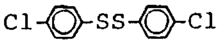
[a] Substrate: 1 mmol, liquid ammonia: 10 ml.
[b] Isolated yield based on the substrate.
[c] 4-Nitrophenyl-substituted phenyl sulfide is present in trace amounts.

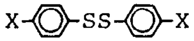

1a-j
⁻SSNH2
O2N
X
Y
Z
O2N-⟨⟩-SSNH2
(Z-S⁻ ↔ Z-S-X⁻)
S8-NH3
O2N-⟨⟩-S⁻
Z-S⁻
O2N-⟨⟩-SS-⟨⟩-NO2
4
O2N-⟨⟩-SS-Z
2a-d
Z-SS-Z
3a-d
X = NH, NTs, Y = NH, Z = -⟨⟩-CH3, -⟨⟩, -⟨⟩-Cl, ⟨N⟩

SCHEME 1

TABLE II

Formation of unsymmetrical aromatic disulfides from symmetrical aromatic disulfide in liquid ammonia

Run[a]	Disulfide 	React. Temp/°C	S_8/mg atom	Yield of Product/%[b] 
1		40	2	35
2		60	2	37
3		40	0	25
4		20	2	31
5		100	2	24
6		20	0	29

[a] Substrate (): 1 mmol, Disulfide (): 1 mmol, Liquid Ammonia: 10 ml, Reaction Time: 2 h.
[b] Isolated yield based on substrate.

As shown in Table II, unsymmetrical disulfides were formed by the reaction of symmetrical disulfides in liquid ammonia. Although in this reaction the effect of elemental sulfur in liquid ammonia is still obscure, we were able to confirm the direct formation of unsymmetrical aromatic disulfide from the symmetrical aromatic disulfide in liquid ammonia, that is, sulfide exchange was observed. Accordingly, there are two pathways for the formation unsymmetrical aromatic disulfide as shown in Scheme 1 and Eq. (2).

As mentioned above, we obtained the unsymmetrical aromatic disulfide by the reaction of aromatic sulfides and related compounds with elemental sulfur in liquid ammonia in moderate yields. It is especially noteworthy that unsymmetrical aromatic disulfides are formed in such a polar basic solvent as liquid ammonia.

EXPERIMENTAL

Materials. Liquid ammonia: Commercially available liquid ammonia (Mitsubishi Gas-Kagaku Co.) was used after one distillation.

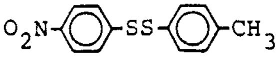
Elemental Sulfur: Commercial material (Kanto Chemical Co.) was used after recrystallization from carbon disulfide.

Substrate: Sulfides (**1a–c**), sulfimides (**1d–h**) and sulfodiimides (**1i–j**) were synthesized by known procedures.[10]

Reaction Vessel. An all-titanium autoclave was used to avoid corrosion with elemental sulfur in liquid ammonia.

Reactions. Reaction of 4-Nitrophenyl-Substituted Phenyl Sulfides, *S*-4-Nitrophenyl Substituted Phenyl Sulfimides and *S*-4-Nitrophenyl *S*-Substituted Phenyl Sulfodiimides with Elemental Sulfur in Liquid Ammonia: Substrate (1 mmol) and elemental sulfur (1 mg atom) were introduced into the titanium autoclave (volume of 50 ml). After evacuation, liquid ammonia (10 ml) was charged into the autoclave. The mixture of substrate and elemental sulfur in liquid ammonia was allowed to react with stirring. The reaction was worked up by evaporation of ammonia and then the reaction mixtures obtained were chromatographed on silica gel (Wako gel C-300) using chloroform as eluent. The products, unsymmetrical (**2a–d**) and symmetrical (**3a–d** and **4**) disulfides, were identified by means of authentic samples.[11] The

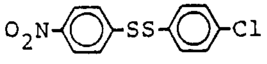
NMR spectran data of the unsymmetrical disulfides were as follows:



2a

: NMR($CDCl_3$)

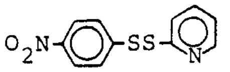
δ = 8.16 (2 H, d, J = 8.3 Hz, arom)
7.67 (2 H, d, J = 7.9 Hz, arom)
7.44 (2 H, d, J = 8.3 Hz, arom)
7.12 (2 H, d, J = 7.9 Hz, arom)
2.28 (3 H, s, Methyl)



2b

: NMR($CDCl_3$)

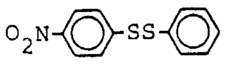
δ = 8.11 (2 H, d, J = 8.4 Hz, arom)
7.57 (2 H, d, J = 8.4 Hz, arom)
7.36 (2 H, d, J = 8.6 Hz, arom)
7.22 (2 H, d, J = 8.6 Hz, arom)



2c

: NMR($CDCl_3$)

δ = 8.70 (1 H, m, arom)
8.35 (2 H, d, J = 9.0 Hz, arom)
7.84 (1 H, m, arom)
7.72 (2 H, d, J = 9.0 Hz, arom)
7.20–7.50 (2 H, m, arom)



2d

: NMR($CDCl_3$)

δ = 8.12 (2 H, d, J = 8.2 Hz, arom)
7.60 (2 H, d, J = 8.2 Hz, arom)
7.20–7.70 (5 H, m, arom)

The elemental analysis of the products were as follows: **2a**, Found: C, 56.56; H, 3.87; N, 5.31. Calcd for $C_{13}H_{11}NO_2S_2$: C, 56.30; H, 4.00; N, 5.05. **2b**, Found: C, 48.11; H, 2.99; N, 4.86. Calcd for $C_{12}H_8NO_2S_2Cl$: C, 48.40; H, 2.71; N, 4.70. **2c**, Found: C, 50.13; H, 3.28; N, 10.77. Calcd for $C_{11}H_8N_2O_2S_2$: C, 49.99; H, 3.05; N, 10.60. **2d**, Found: C, 54.99; H, 3.41; N, 5.15; Calcd for $C_{12}H_9NO_2S_2$: C, 54.73; H, 3.44; N, 5.32. **3a**, Found: C, 68.51; H, 5.60. Calcd for $C_{14}H_{14}S_2$: C, 68.25; H, 5.73. **3b**, Found: C, 50.47; H, 2.53. Calcd for $C_{12}H_8S_2Cl_2$: C, 50.18; H, 2.81. **3c**, Found: C, 54.69; H, 3.48; N, 12.93. Calcd for $C_{10}H_8N_2S_2$: C, 54.52; H, 3.66; N, 12.72. **3d**, Found: C, 65.83; H, 4.76. Calcd for $C_{12}H_{10}S_2$: C, 66.02; H, 4.62. **4**, Found: 46.52; H, 2.41; N. 9.36. Calcd for $C_{12}H_8N_2O_4S_2$: C, 46.75; H, 2.62; N, 9.09.

Reaction of 4,4′-Dinitrodiphenyl Disulfide with 4,4′-Disubstituted Diphenyl Disulfide in Liquid Ammonia: 4,4′-Dinitrodiphenyl disulfide (1 mmol) and 4,4′-disubstituted diphenyl disulfides (1 mmol) were taken into the titanium autoclave. After evacuation, liquid ammonia (10 ml) was charged into the autoclave. After work up by evaporation of ammonia, the reaction mixture was chromatographed on silica gel (Wako gel C-300) using chloroform as eluent. The products obtained were identified by comparing the NMR, IR and Mass spectra with those of authentic samples.[11]

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