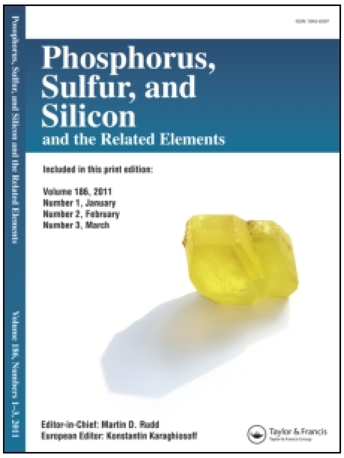

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REACTION OF 4-NITROPHENYL 4'-NITROBENZENETHIOLSULFONATE WITH LIQUID AMMONIA

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REACTION OF 4-NITROPHENYL 4′-NITROBENZENETHIOLSULFONATE WITH LIQUID AMMONIA

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4-Nitrophenyl 4′-nitrobenzenethiolsulfonate (**1**) reacted readily with liquid ammonia at room temperature to afford 4-nitrobenzenesulfenamide (**2**) and ammonium 4-nitrobenzenesulfinate (**3**). The products, (**2**) and (**3**), were found to react with liquid ammonia eventually affording various compounds, such as 4-nitroaniline (**4**), 4,4′-dinitrodiphenyl disulfide (**5**), 4,4′-dinitrodiphenyl sulfide (**6**), ammonium 4-nitrobenzenethiosulfonate (**7**), 4-nitrobenzenethiol (**8**) and 4-nitrophenyl 4′-aminophenyl sulfide (**9**). A reactive nucleophile, "$H_2NS_x^-NH_4^+$," which is formed upon dissolving elemental sulfur, S_8, in liquid ammonia, appears to play an important role in this reaction as in the reaction of 4-nitrobenzenesulfenamide with elemental sulfur in liquid ammonia.[1]

INTRODUCTION

Earlier Dunbar and Rodgers pointed out that the reaction of thiolsulfinate with amines was a reversible reaction in which the nucleophile, i.e. morpholine, piperidine, diethylamine, ethyleneimine, cyclohexylamine, etc. attacks the sulfenyl sulfur, except in the case of trichloromethyl 4-toluenethiolsulfonate, to give the corresponding sulfenamides.[2]

Kice also studied the kinetics of the reaction between phenyl benzenethiolsulfonate with piperidine, piperazine, hydrazine, butylamine, morpholine, hydroxylamine and aminoethyl acetate and revealed the reaction to be of first order dependence on both the substrate and the nucleophile.[3] These reactions are usually completed in one step and the ultimate products were the corresponding sulfenamides.

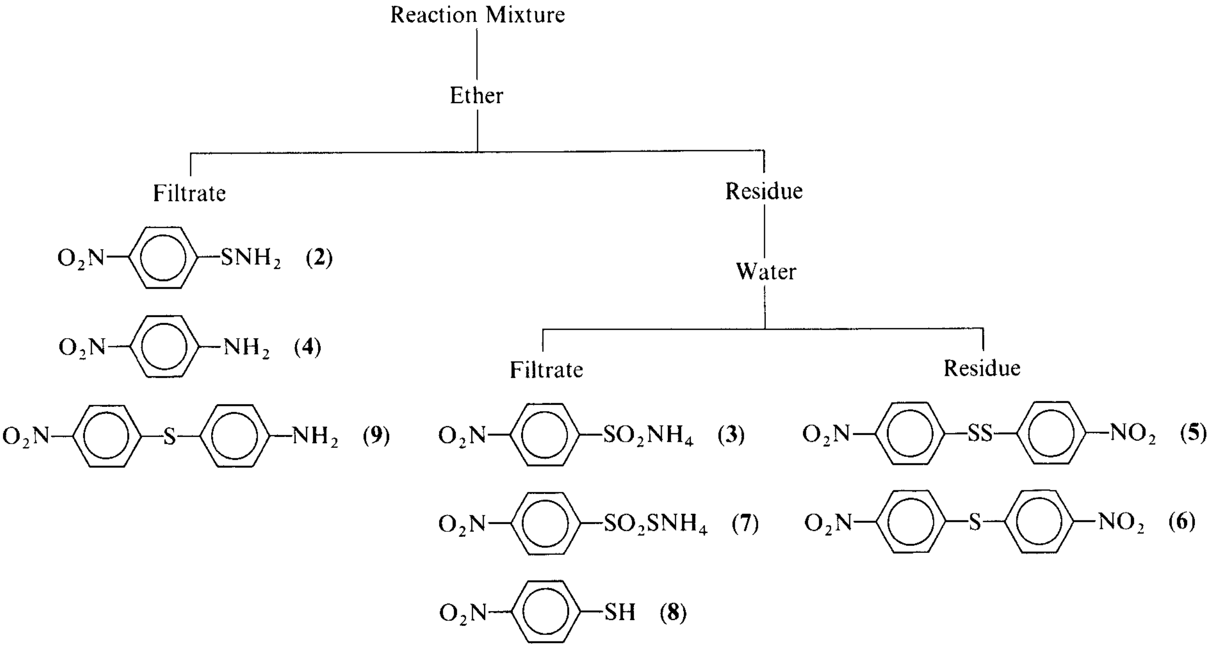
In the reaction of the 4-nitrophenyl 4′-nitrobenzenethiolsulfonate (**1**) with liquid ammonia, however, we obtained not only the initial reaction products, i.e., 4-nitrobenzenesulfenamide (**2**) and ammonium 4-nitrobenzenesulfinate (**3**), but also various other products, such as 4-nitroaniline (**4**), 4,4′-dinitrodiphenyl disulfide (**5**), 4,4′-dinitrodiphenyl sulfide (**6**), ammonium 4-nitrobenzenethiosulfonate (**7**), 4-nitrobenzenethiol (**8**) and 4-nitrophenyl 4′-aminophenyl sulfide (**9**), which are obviously derived from the 4-nitrobenzenesulfenamide (**2**) and ammonium 4-nitrobenzenesulfinate (**3**). Thus we have studied the reaction of 4-nitrobenzenesulfenamide (**2**) with liquid ammonia in connection with the reaction of ammonium 4-nitrobenzenethiosulfonate (**7**) and ammonium 4-nitrobenzenesulfinate (**3**) with liquid ammonia.

EXPERIMENTAL

Materials

4-Nitrophenyl 4′-nitrobenzenethiolsulfonate (**1**) was prepared by oxidation of 4,4′-dinitrodiphenyl disulfide[4] with perbenzoic acid in chloroform according to a known procedure.[5,6] mp. 182°C; NMR ($CDCl_3$) δ = 8.30 (2H, d, J = 9.2Hz, aromatic), 8.22 (2H, d, J = 9.2Hz, aromatic), 7.79 (2H, d, J = 9.2Hz, aromatic) and 7.61 (2H, d, J = 9.2Hz, aromatic); MS (70eV), m/e, 340.

Reaction of the thiolsulfonate (**1**) *with liquid ammonia* Thiosulfonate (**1**), 0.85g (2.5 mmol) was placed in an all titanium autoclave of 50 ml. capacity into which a measured amount of



SCHEME I

liquid ammonia was charged under cooling with ice-salt. The reaction conditions were chosen arbitarily (reaction temperature and time). After removing ammonia, the reaction mixtures were separated by the scheme I.

The yields of the products were estimated by the proton NMR intensities of the *m*-protons of the nitro-derivatives in each step of the separation scheme. All the products were identified by comparing the IR and NMR and other physical properties with those of authentic known samples.[7]

Reaction of ammonium 4-nitrobenzenesulfinate (**3**) *and 4-nitrobenzenethioulfonate* (**7**) *with liquid ammonia* These reactions were also carried out in the same manner as in the reaction of 4-nitrophenyl 4′-nitrobenzenethiolsulfonate (**1**) with liquid ammonia.

Reaction of ammonium 4-nitrobenzenesulfinate (**3**) *with elemental sulfur in liquid ammonia* Ammonium 4-nitrobenzenesulfinate (**3**) 0.51 g and 0.12 g of elemental sulfur were placed in an all titanium autoclave. After evacuation, 30 ml. of liquid ammonia was charged and the reaction was allowed to proceed under vigorous stirring. The separation of the reaction mixture was carried out according to the scheme I.

Reaction of ammonium 4-nitrobenzenesulfinate (**3**) *and ammonium 4-nitrobenzenethiosulfonate* (**7**) *with 4,4′-dinitrodiphenyl sulfide* (**6**) *in liquid ammonia* These reactions were also carried out as above.

Spectral Data and Analysis

4-Nitrobenzenesulfenamide (**2**) mp. 105°C; IR (KBr) 3370 and 3285 (—NH_2); NMR ($CDCl_3$) $\delta = 8.15$ (2H, d, J = 9.2 Hz, aromatic), 7.42 (2H, d, J = 9.2 Hz, aromatic) and 2.76 (2H, —NH_2); MS (70eV), m/e, 170; (Found: S, 18.4%, Calcd.: S, 18·8%).

Ammonium 4-nitrobenzenesulfinate (**3**) IR (KBr) 3000 (NH_4^+) and 1040 cm^{-1} (—SO_2—); NMR (CD_3SOCD_3) $\delta = 8.20$ (2H, d, J = 8.0 Hz, aromatic), 7.70 (2H, d, J = 8.0 Hz, aromatic) and 7.27 (4H, NH_4^+) (Found: S, 15.7% Calcd. S, 15.7%).

4-Nitroaniline (**4**) mp. 145°C; IR (KBr) 3470 and 3350 cm^{-1} (NH_2); NMR ($CDCl_3$) $\delta = 8.07$ (2H, d, J = 8.0 Hz, aromatic), 6.64 (2H, d, J = 8.0 Hz, aromatic) and 4.40 (2H, s, —NH_2).

4,4′-Dinitrodiphenyl disulfide (**5**) mp. 181°C; NMR ($CDCl_3$) $\delta = 8.23$ (2H, d, J = 9.0 Hz, aromatic) and 7.66 (2H, d, J = 9.0 Hz, aromatic).

4,4′-Dinitrodiphenylsulfide (**6**) mp. 154°C; NMR ($CDCl_3$) $\delta = 8.23$ (2H, d, J = 9.2 Hz, aromatic) and 7.51 (2H, d, J = 9.2 Hz, aromatic).

4-Nitrophenyl 4′-aminophenyl sulfide (**9**) mp. 142°C; IR (KBr) 3470 and 3380 cm^{-1} (—NH_2); NMR ($CDCl_3$) $\delta = 8.03$ (2H, d, J = 9.2 Hz, aromatic), 7.35 (2H, d, J = 9.2 Hz, aromatic), 7.11 (2H, d, J = 8.6 Hz, aromatic), 6.76 (2H, d, J = 8.6 Hz, aromatic) and 3.92 (2H, s, aromatic).

Ammonium 4-nitrobenzenethiosulfonate (**7**) IR (KBr) 1180 (—SO_2—) and 3100 cm^{-1} (NH_4^+); NMR (CD_3SOCD_3) $\delta = 8.25$ (2H, d, J = 8.4 Hz, aromatic), 7.96 (2H, d, J = 8.4 Hz, aromatic) and 7.12 (4H, s, NH_4); (Found: S, 25.2%, Calcd. S, 27.1%).

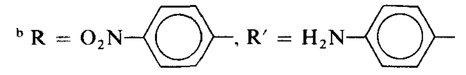
4-Nitrobenzenethiol (**8**) mp. 78°C; IR (KBr) 2540 (—SH); NMR ($CDCl_3$) $\delta = 8.10$ (2H, d, J = 8.6 Hz, aromatic), 7.36 (2H, d, J = 8.6 Hz, aromatic) and 3.66 (1H, s, —SH).

TABLE I

Effect of reaction temperature[a]

Run	Temp. (°C)	Yield of product[bc] R—SNH$_2$	R—SO$_2$NH$_4$	R—NH$_2$	R—SS—R	R—S—R	R—S—R′	R—SO$_2$SNH$_4$	R—SH
1	60	49	49	trace	trace	—	—	—	—
2	80	—	15	28	12	25	—	20	trace
3	100	—	4	10	6	48	12	15	5

[a] 4-Nitrophenyl 4′-nitrobenzenethiolsulfonate (**1**): 0.85 g (2.5 mmol), liquid ammonia: 30 ml., reaction time: 4hr. substrate concentration: 0.083 mol/l.

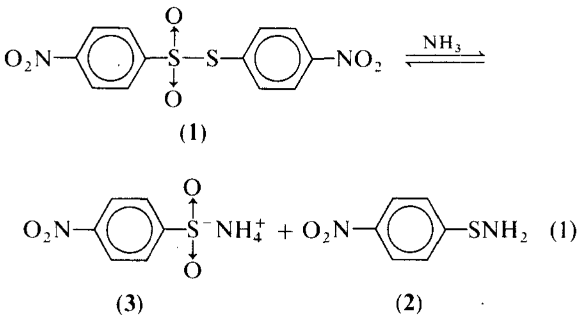
[b] 

[c] Percent of recovered benzene ring. Yields are relative since only external TMS standard was used.

RESULTS AND DISCUSSION

In the reaction of 4-nitrophenyl 4′-nitrobenzenethiolsulfonate (**1**) with liquid ammonia, the products obtained were 4-nitrobenzenesulfenamide (**2**), ammonium 4-nitrobenzenesulfinate (**3**), 4-nitroaniline (**4**) 4,4′-dinitrodiphenyl disulfide (**5**), 4,4′-dinitrodiphenyl sulfide (**6**), ammonium 4-nitrobenzenethiosulfonate (**7**), 4-nitrobenzenethiol (**8**) and 4-nitrophenyl 4-aminophenyl sulfide (**9**), among which (**2**) and (**3**) are the initial reaction products and (**4**)–(**9**) are those of the subsequent reactions. The yields of these products varied with the reaction temperature, time and substrate concentration; they are listed in Tables I, II and III, respectively.

The initial reaction is undoubtedly the nucleophilic substitution on the sulfenyl sulfur of the thiolsulfonate (**1**) with liquid ammonia as shown below.



(1)

(3) (2)

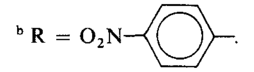
This reaction is so fast that the starting substrate disappeared immediately affording the sulfenamide (**2**) and the sulfinate (**3**) quantitatively in the initial part of the reaction, as shown in Tables I and

TABLE II

Effect of reaction time[a]

Run	Time (min)	Yield of product[bc] R—SNH$_2$	R—SO$_2$NH$_4$	R—NH$_2$	R—SS—R	R—S—R	R—SO$_2$SNH$_4$	R—SH
1	240	49	49	trace	trace	—	—	—
2	300	45	49	2	4	—	—	—
3	330	33	43	9	10	—	5	—
4	360	3	17	33	11	3	31	2
5	420	—	12	40	8	4	33	3

[a] 4-Nitrophenyl 4′-nitrobenzenethiolsulfonate (**1**): 0.85 g (2.5 mmol), liquid ammonia: 30 ml, substrate concentration: 0.083 mol/l.

[b] 

[c] Percent of recovered benzene ring. Yields are relative since only external TMS standard was used.

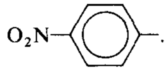
TABLE III

Effect of substrate concentration[a]

Run	Conc. (mol/l)	Temp. (°C)	Yield of product[bc]					
			R—SNH_2	R—SO_2NH_4	R—NH_2	R—SS—R	R—S—R	R—SO_2SNH_4
1	0.074	60	49	49	trace	trace	—	—
2	0.111	60	—	18	37	12	trace	32
3	0.222	60	—	10	40	5	4	38
4	0.444	60	—	trace	44	trace	6	48
5	0.230	40	50	50	—	—	—	—
6	0.460	40	—	6	41	6	4	42

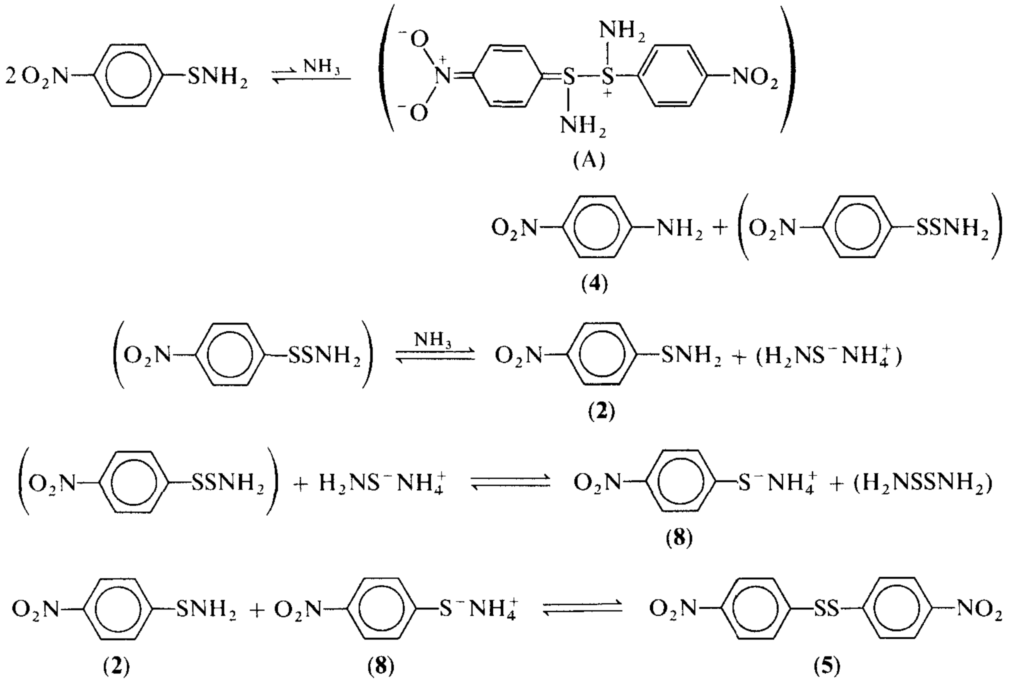
[a] 4-Nitrophenyl 4′-nitrobenzenethiolsulfonate (**1**): 0.85 g (2.5 mmol). The amount of liquid ammonia was varied. React. time: 240 min.

[b] R =



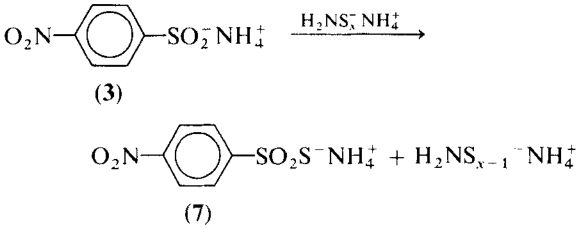
[c] Percent of recovered benzene ring. Yields are relative since only external TMS standard was used.

II, which also indicate that the amounts of the sulfenamide (**2**) and ammonium 4-nitrobenzenesulfinate (**3**) decreased when the reaction temperature was raised. The sulfenamide (**2**) and the sulfinate (**3**) reacted further to yield other products, such 4-nitroaniline (**4**), 4-nitrobenzenethiol (**8**), etc., as shown in Tables I and II. The results in Table III suggest that this reaction depends on the concentration of the thiolsulfonate (**1**), (see runs 1–4), and there was an induction period (see runs 5–6). We also observed the same phenomenon in our previous study on the reaction of 4-nitrobenzenesulfenamide (**2**) with liquid ammonia, and suggested the possible involvement of the sulfonium species (A) as a key but unobservable intermediate for the reaction of the sulfenamide (**2**) with liquid ammonia as shown in Scheme II[1]



SCHEME II

The formation of 4-nitroaniline (**4**) was rationalized previously on the assumption of the sulfonium intermediate. Formation of the compound (**7**) in this reaction is rather interesting, since it suggests the involvement of elemental sulfur. Probably, the compound (**7**) was formed by the reaction of ammonium 4-nitrobenzenesulfinate (**3**) with the thiohydroxyamines "$H_2NS_x^-$" ($x = 1 - 8$) which can be formed upon mixing elemental sulfur and liquid ammonia. Actually, we obtained ammonium 4-nitrobenzenethiosulfonate (**7**) by treatment of ammonium 4-nitrobenzenesulfinate (**3**) with elemental sulfur-liquid ammonia, S_8—NH_3.



Apparently elemental sulfur dissociates in the liquid ammonia as shown below.[8]

$$S_8 \overset{NH_3}{\rightleftharpoons} H_2NS{-}S_6{-}S^-NH_4^+$$

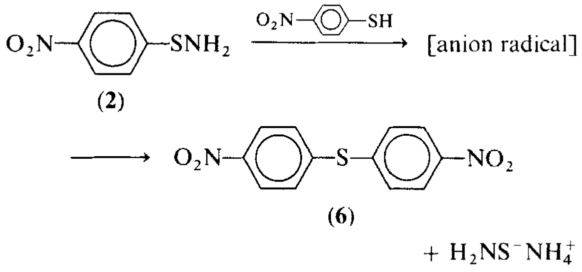
$$H_2NS{-}S_6{-}S^-NH_4^+ \overset{NH_3}{\rightleftharpoons} 2H_2NS{-}S_2{-}S^-NH_4^+$$

$$H_2NS{-}S_2{-}S^-NH_4^+ \overset{NH_3}{\rightleftharpoons} 2H_2NS{-}S^-NH_4^+$$

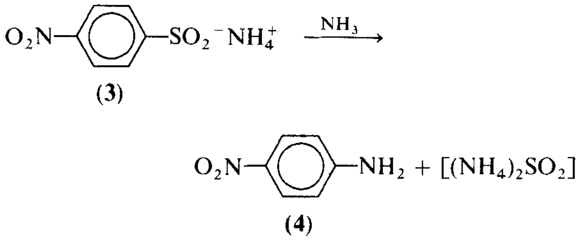
$$H_2NS{-}S^-NH_4^+ \overset{NH_3}{\rightleftharpoons} 2H_2NS^-NH_4^+$$

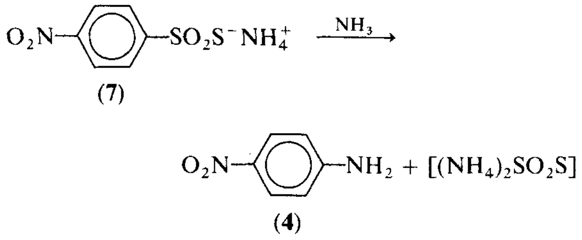
The formation of a new nucleophile "$H_2NS^-NH_4^+$" seems to be quite important, since the new species "$H_2NS^-NH_4^+$" is considered to be a strong nucleophile and hence would play an important role in the nucleophilic reaction of the sulfenamide (**2**) with liquid ammonia.

The formation of 4,4′-dinitrodiphenyl sulfide (**6**) was probably due to the one-electron transfer reaction of aromatic nitro compounds, e.g., the reaction of 4-nitrobenzenesulfenamide (**2**) with 4-nitrobenzenethiol (**8**) in liquid ammonia as shown below.



Although ammonium 4-nitrobenzenethiosulfonate (**7**) is formed from ammonium 4-nitrobenzenesulfinate (**3**), the combined yield of the sulfinate (**3**) and the thiosulfonate (**7**) does not exceed 50% (see Table I), due undoubtedly to the subsequent reactions which lead to the formation of 4-nitroaniline (**4**) and other products. Thus the reactions of ammonium 4-nitrobenzenesulfinate (**3**) and ammonium 4-nitrobenzenethiosulfonate (**7**) with liquid ammonia were carried out and the results of the reactions shown in the following equations are listed in the Table IV.



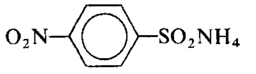
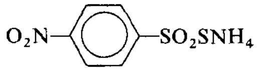


The results in Table IV seem to comfirm the occurence of subsequent reactions of the sulfinate (**3**) and the thiosulfonate (**7**) with liquid ammonia. The sulfinate (**3**) reacted faster than the thiosulfonate (**7**), as in many nucleophilic reactions.[10]

The formation of 4-nitrophenyl 4′-aminophenyl sulfide (**9**) is not surprising, since ammonium thiosulfate can reduce the nitro group and is present in this system, together with ammonium sulfoxylate, $(NH_4)_2SO_2$, and $H_2NS_x^-NH_4^+$($x = 1 - 8$). Actually, we observed the reduction of the nitro group of the sulfide (**6**) upon treating the sulfide (**6**) with the sulfinate (**3**) and thiosulfonate

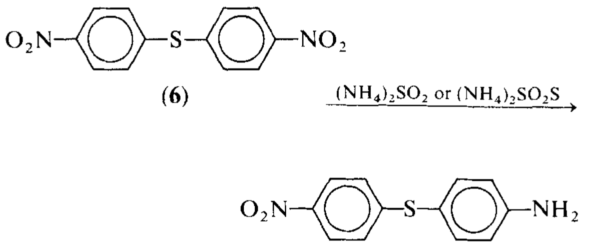
TABLE IV

Reaction of 4-nitrobenzenesulfinate 3 and 4-nitrobenzenethiosulfonate (7) with liquid ammonia.

	Yield of 4-nitroaniline (**4**)[b]			
Substrate[a]	40°C	60°C	80°C	100°C
 (3)	trace	6	16	35
 (7)	—	3	—	14

[a] Substrate: 0.85 g (2.5 mmol), liquid ammonia: 30 ml.
[b] Yields are relative since only external TMS standard was used.

(7) in liquid ammonia. These results are shown in the Table V.



The reduction of aromatic nitro compounds also took place with $H_2NS_x^-NH_4^+$, as shown below.

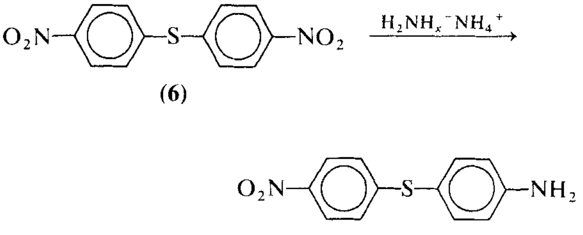
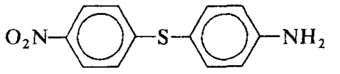
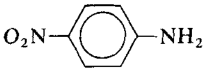
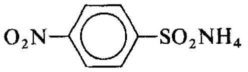
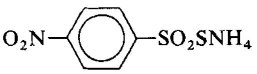
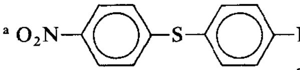
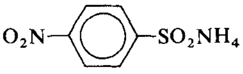
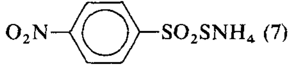


TABLE V

Reaction of 4,4′-dinitrodiphenyl sulfide (**6**) with 4-nitrobenzenesulfinate (**3**) and 4-nitrobenzenethiosulfonate (7) in liquid ammonia[a]

	Yield of product[b]	
Reagent		
	20	30
	trace	7

[a]  (**6**): 0.345 g (1.25 mmol),  (**3**): 0.510 g (2.50 mmol),  (7) 0.590 g (2.50 mmol), React. temp.: 100°C, time: 240 min.
[b] Percent of recovered benzene ring. Yields are relative since only external TMS standard was used.

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