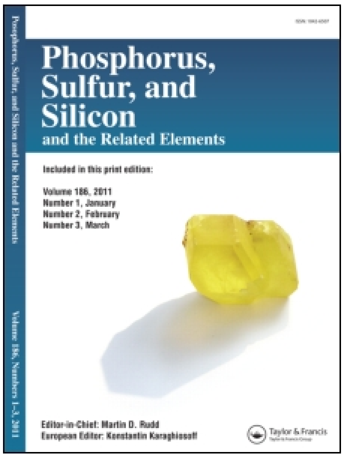

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REACTION OF 4,4′-DINITRODIPHENYL DISULFIDE WITH LIQUID AMMONIA

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4,4′-Dinitrodiphenyl disulfide (**1**) reacted with liquid ammonia to give 4-nitrobenzenesulfenamide (**2**) and 4-nitrobenzenethiol (**3**). The 4-nitrobenzenesulfenamide (**2**) thus formed reacted further with liquid ammonia to afford 4-nitroaniline (**4**) unexpectedly at relatively low temperatures. The unexpected reaction is presumed to proceed via the formation of a sulfonium intermediate (**7**).

The S–S bond in disulfides is readily cleaved by such nucleophiles[1] as cyanide,[2] phosphines,[3] thiols,[4] amines[5] and hydroxide[6] in the following manner (Eq. 1) and there have been numerous investigations on the mechanisms of these reactions.[7]

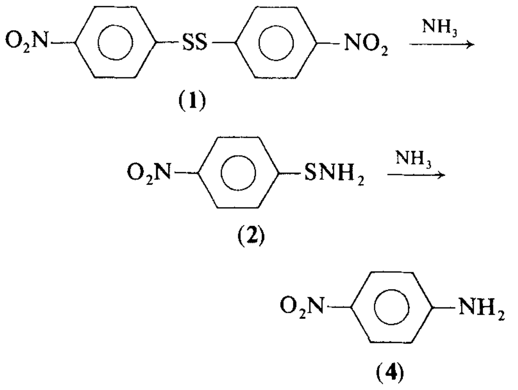
$$\text{R–SS–R} \overset{\text{Nu}^-}{\rightleftharpoons} \text{R–SNu} + \text{R–S}^- \qquad (1)$$

However, since most of these are reversible reactions, it is difficult to observe only one particular side of the reaction when the equilibrium is attained very rapidly; for example, the reaction between aromatic disulfides and amines. In many cases, the reaction is stopped by either quenching or removing the products, i.e. R–SNu or R–S$^-$ in Eq. (1).

Meanwhile, numerous methods have been developed for the syntheses of sulfenamides, e.g. oxidative condensation of thiols with amines,[8] aminolysis of alkylsulfenylthiocyanates or thiophthalimides[9] and pyrolysis of sulfimides.[10] The relatively weak bond in the sulfenamide may be attributed to the rather strong repulsive electron interaction between two hetero atoms bearing lone electron pairs[11] which overwhelm the possible small attractive (*p–d*) π conjugation.[12]

Recently, Davis and his coworkers showed that aliphatic and aromatic sulfenamides were nicely obtained by the aminolysis of aliphatic and aromatic disulfides with either alkylamines or ammonia in the presence of silver nitrate in methanol,[13] where silver nitrate is presumed to react with the thiolate anion to yield the insoluble mercaptides, R–SAg. The formation of the mercaptide apparently shifted the equilibrium to the right and hence the sulfenamides were obtained quantitatively.

We also found that ammonolysis of 4,4′-dinitrodiphenyl disulfide (**1**) resulted in the formation of 4-nitrobenzenesulfenamide (**2**), which upon treating with liquid ammonia reacted further and yielded 4-nitroaniline (**4**), as was reported in our previous paper on the reaction of 4-nitrobenzenesulfenamide (**2**) with liquid ammonia.[14]

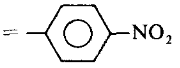


(2)

Aniline (**4**) was found to be formed in the reaction of the disulfide (**1**) with liquid ammonia more readily than the reaction of the sulfenamide (**2**) with liquid ammonia, while the formation of 4-nitroaniline (**4**) from 4-nitrobenzenesulfenamide (**2**) was found to be catalyzed by either 4-nitrobenzenethiol (**3**) or 4,4'-dinitrodiphenyl disulfide (**1**). This paper describes these reactions.

TABLE I

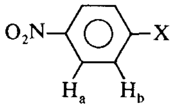
Chemical shifts of reaction products[a]

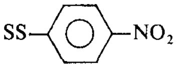
Product		Chemical shift (ppm)		
R = 		Aromatic proton[c]		Other proton
		H_a	H_b	
R—SS—R	1	8.23	7.66	
$R—SNH_2$	2	8.15	7.42	$2.76\ (—NH_2)$
R—SH	3	8.10	7.36	3.66 (—SH)
$R—NH_2$	4	8.07	6.64	$4.40\ (—NH_2)$
R—S—R	5	8.23	7.51	

[a] Instrument: HITACHI R-22 (90 MHz).

[b] The chemical shifts were measured in $CDCl_3$ as solvent using TMS as standard.

[c] The aromatic protons H_a and H_b are the following:

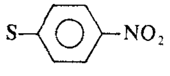


(**1**): X = SS 

(**2**): $X = S—NH_2$

(**3**): X = SH

(**4**): $X = NH_2$

(**5**): X = S 

EXPERIMENTAL

Reaction Vessel. A titanium autoclave was used for all the reactions since titanium is quite inert to any of the sulfur species in this system and also does not react with $S_8—NH_3$ which corroded stainless steel.

Materials

Ammonia. Liquid ammonia was distilled just before use. 4,4'-Dinitrodiphenyl disulfide (**1**): The disulfide (**1**) was prepared by treating 4-nitrochlorobenzene with sodium disulfide in refluxing ethanol[15] and recrystallized several times from chloroform; mp 180°C.

Sodium disulfide. Sodium disulfide was prepared from sodium tetrasulfide and sodium monosulfide; namely, 3 mol. of sodium disulfide was obtained when a mixture of 1 mol. of sodium tetrasulfide and 2 mol. of sodium monosulfide in aqueous solution were cooled with stirring and recrystallized from water. (Sodium tetrasulfide and sodium monosulfide were the products of Sankyo-Kasei Co. Osaka, Japan.)

Reaction of 4,4'-dinitrodiphenyl disulfide (**1**) *with liquid ammonia.* Liquid ammonia, 20 ml, was charged into a titanium autoclave containing 2.5 mmol. 0.77 g) of 4,4'-dinitrodiphenyl disulfide (**1**). After allowing the disulfide (**1**) to react under the respective conditions shown in Tables 2 and 3, the whole reaction mixture was at once placed into a flask. Then, about 30 ml of diethyl-ether was immediately added to the flask. After evaporation of ammonia, the ethereal solution was filtered. Ether was then allowed to evaporate and a mixture of the sulfenamide (**2**), aniline (**4**) and a slight amount of the disulfide (**1**) (at low temperature such as 20°C) or 4,4'-dinitrodiphenyl sulfide (**5**) (at high temperature such as 60°C) was obtained. The mixture was washed with about 20 ml of water. The solution was acidified with aq. HCl solution and then extracted with 30 ml of ether. From the ether layer, 4-nitrobenzenethiol (**3**) was obtained. The sulfide (**5**) and the disulfide (**1**) were obtained from the residue. The yields of these products were determined by measuring the nmr intensities of the aromatic meta protons of the nitrophenyl group and identified by comparing the ir, nmr and mp with those of the authentic samples. These chemical shifts are shown in Table I.

4-Nitrobenzenethiosulfenamide (**6**) was not observed in this reaction. However, since the compound is an important intermediate, it was synthesized by the following method and characterized.[16] An equimolar amount of sulfur dichloride was added dropwise into the solution of 4-nitrobenzenethiol in ether at 0°C. After the addition, insoluble materials were removed and the solution containing 4-nitrobenzenethiosulfenyl chloride, $p\text{—}O_2N—C_6H_4—SSCl$, was cooled at 0°C. Ammonia gas was passed into the solution until ammonium chloride no longer formed. Ammonium chloride thus formed was removed by filtration and the ether was evaporated under vacuum. The reddish brown material obtained was recrystallized from benzene–hexane mixture several times. The rather unstable 4-nitrobenzenethiosulfenamide (**6**) was identified on the basis of the following characteristics: mp 86°C; ir (KBr) 3290 and 3390 (N—H) cm^{-1}; nmr ($CDCl_3$) $\delta = 8.18$ (2H, d, $J = 9$ Hz), 7.70 (2H, d, $J = 9$ Hz) and 3.29 (2H, broad, NH_2); Found 6: S, 32.0%. Calcd. for $C_6H_6O_2S_2$; S, 31.7%. The compound (**6**) was found to disproportionate readily to 4,4'-dinitrophenyl disulfide (**1**) upon heating or irradiation with light.

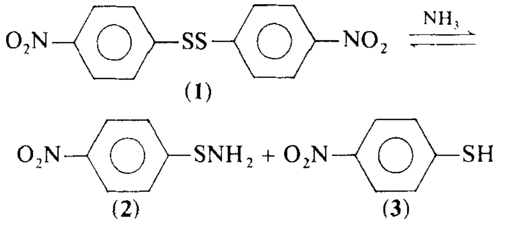
4-Nitrobenzenethiosulfenamide (**6**) reacted readily with ammonia to give 4-nitrobenzenethiol (**3**), 50%; 4,4'-dinitrodiphenyl disulfide (**1**), 20%; and a very small amount of 4-nitroaniline (**4**) at 20°C for 2 hr. Moreover, 4-nitrobenzenethiosulfenamide (**6**) also reacted readily with 4-nitrobenzenethiol (**3**) in liquid ammonia to give 4,4'-dinitrodiphenyl disulfide (**1**), 58%, and a very small amount of 4-nitroaniline (**4**) at 20°C for 1 h (see Eqs. 6–8). These two reactions are similar to the reaction of 4-nitrobenzenesulfenamide (**2**) with ammonia and 4-nitrobenzenethiol (**3**). However, the formation of 4-nitroaniline (**4**) from 4-nitrobenzenesulfenamide (**2**) by further reaction was easier than that from thiosulfenamide (**6**).

RESULTS AND DISCUSSION

In the reaction of 4,4'-dinitrodiphenyl disulfide (**1**) with ammonia in methanol in the presence of silver nitrate, 4-nitrobenzenesulfenamide (**2**) and 4-nitrobenzenethiol (**3**) were reported to be obtained by F. A. Davis *et al.*[13] In addition to the sulfenamide (**2**) and the thiol (**3**) we found aniline (**4**) among the products in the reaction of 4,4'-dinitrodiphenyl disulfide (**1**) with liquid ammonia in a titanium autoclave at 20°C. The facile formation of 4-nitroaniline (**4**) is rather surprising, since the aniline (**4**) is a nucleophilic substitution product on the C_1 aryl carbon, of the sulfenamide (**2**), which has a rather poor leaving group, $-SNH_2$, and cannot be considered as reactive as 4-nitrochlorobenzene, which is quite unreactive under the same conditions. The products of the reactions of the disulfide (**1**) with liquid ammonia at 20°C are shown in Table II. Inspection of the data indicates that cleavage of the S—S bond readily occurred by nucleophilic attack of ammonia at 20°C yielding the sulfenamide (**2**) and the thiol (**3**) (Eq. 3)

The facile cleavage of the S—S bond is undoubtedly due to the good leaving ability of 4-nitrobenzenethiolate anion.

Despite the facile cleavage of the S—S linkage, the disulfide (**1**) was found to have remained, clearly implying that the reaction is an equilibrium. The yield of the sulfenamide (**2**) formed by this reaction decreased gradually as the reaction proceeded, since the sulfenamide (**2**) was converted into the aniline (**4**) even at a low temperature such as 20°C; thus the aniline (**4**) gradually increased. Apparently 4-nitroaniline (**4**) is formed from the sulfenamide (**2**) and the formation of aniline (**4**) is catalyzed by the disulfide (**1**) or the thiol (**3**), since the sulfenamide (**2**) alone has no such reactivity in liquid ammonia under these conditions (20°C, substrate: 0.13 mol/l).[14]



(1)

(2) (3)

(3)

TABLE II

Reaction of 4,4′-dinitrodiphenyl disulfide (**1**) with liquid ammonia[a]

Run	Reaction time (min)	Products (%)[b]			
		R–SNH$_2$	R–NH$_2$	R–SH	R–SS–R
1	30	80	0	77	20
2	60	72	trace	82	18
3	90	73	4	77	23
4	120	58	14	72	28
5	150	49	20	69	31
6	180	29	43	72	28
7	210	21	56	77	23
8	240	11	61	72	28
9	270	0	72	72	28
10	420	0	75	75	25

[a] 4,4′-Dinitrodiphenyl disulfide (**1**): 2.5 mmol., Liquid ammonia: 20 ml, Reaction temp.: 20°C.

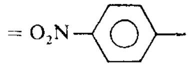
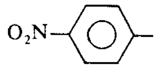
[b] R =


TABLE III

The effect of reaction temperature[a]

Run	Reaction temp. (°C)	Products (%)[b]			
		R–SNH$_2$	R–NH$_2$	R–SH	R–SS–R
1	20	72	trace	82	18
2	30	trace	60	64	36
3	40	0	71	71	29
4	60	0	86	86	14

[a] 4,4′-Dinitrodiphenyl disulfide (**1**): 2.5 mmol., Liquid ammonia: 20 ml, Reaction time: 60 min.

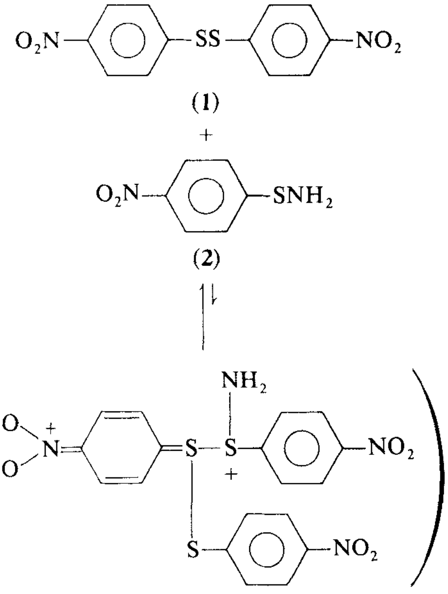
[b] R =


[c] A slight amount of 4,4′-diphenylsulfide (**5**) was contained.

It is interesting to note that the disulfide (**1**) and the thiol (**3**) remained through the reaction even after 420 min (run 10). This suggests that the disulfide (**1**) or the thiol (**3**) is required in this reaction.

Effect of temperature is shown in Table III which reveals that (1) the sulfenamide (**2**) was no longer detected at 40°C, (2) even at 60°C, the disulfide (**1**) remained to be observed (in run 4) and (3) at 60°C, the aniline (**4**) was obtained in a yield of 86%, that is, by elevation of temperature the aniline (**4**) was readily formed from the sulfenamide (**2**).

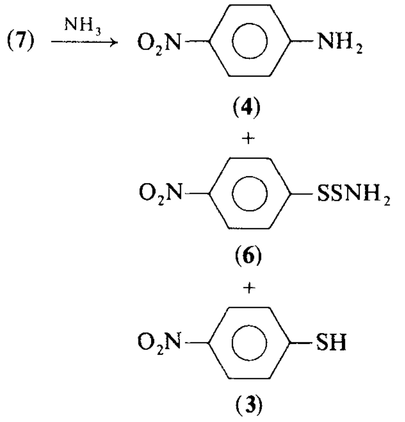
We have suggested earlier a mechanism involving the sulfonium intermediate (**7**) for the formation of



(1)

(2)

(7)



(5)

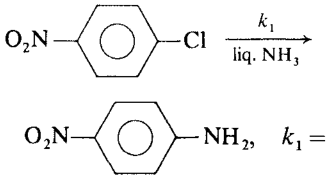
4-nitroaniline (**4**) in the reaction of 4-nitrobenzenesulfenamide (**2**) with liquid ammonia.[14] The same intermediate is apparently involved in this reaction of the disulfide (**1**) with liquid ammonia.

Although we could not detect the formation of the sulfonium intermediate (**7**) directly, the reaction of the sulfenamide (**2**) to yield 4-nitroaniline (**4**) can be explained best by assuming the formation of the sulfonium intermediate (**7**), which has two strong electron-withdrawing groups, $-NO_2$ and $=\underset{|}{S}-\underset{|}{\overset{+}{S}}-$, on a benzene ring to facilitate the nucleophilic attack of ammonia.[15]

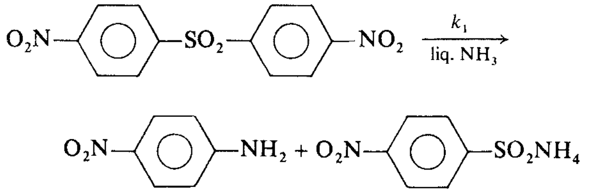
The intermediate (**7**) then would react readily with liquid ammonia to afford 4-nitroaniline (**4**), 4-nitrobenzenethiosulfenamide (**6**) and the thiol (**3**) (Eq. 5).

Incidentally, even 4-nitrochlorobenzene and 4,4′-dinitrodiphenyl sulfone were found to be quite unreactive with liquid ammonia at room temperature and to react very slowly only upon heating as shown below.

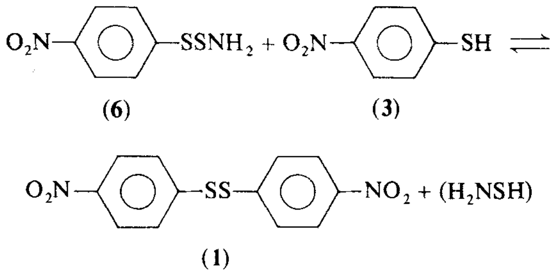
These thiosulfenamide (**6**) thus formed would rapidly react with the thiol (**3**) to give the disulfide (**1**) while with liquid ammonia would afford the thiol (**3**). These reactions are shown together with other reactions of the thiosulfenamide (**6**) in Eq. 6–10, which are all equilibrium reactions.



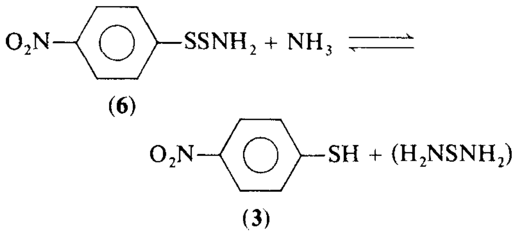
$k_1 = 1.52 \times 10^{-6}$/sec (100°C)



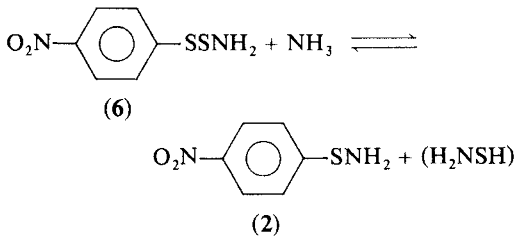
$k_1 = 4.52 \times 10^{-5}$/sec (80°C)



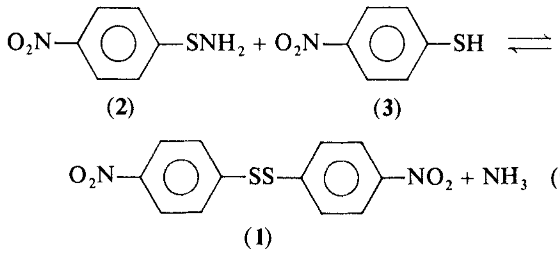
(6)



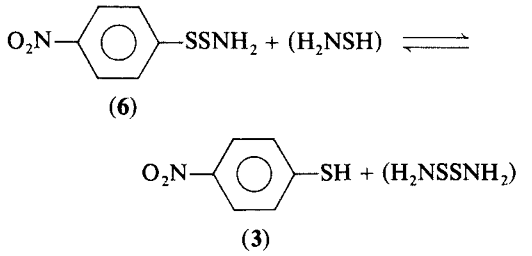
(7)



(8)



(9)



(10)

Since the amount of the thiol (**3**) is relatively large in this system, the reaction shown by Eq. (**6**) was actually observed and only the disulfide (**1**) was obtained, while the thiosulfenamide (**6**) underwent further reaction and was not observed.

Regeneration of the disulfide (**1**) via the reactions (Eqs. 6 and 9) is quite reasonable in view of the facile reactions of the thiosulfenamide (**6**) and the sulfenamide (**2**) with thiol (**3**) found separately.

All these equilibrium reactions appear to take place very rapidly, only the formation of 4-nitroaniline (**4**) being rather slow. Thus the results shown in Table II and III were obtained.

In addition, the new nucleophile, "H_2NSH," thiohydroxylamine, can be readily obtained by treating elemental sulfur, S_8, in liquid ammonia; its behavior is totally unknown.[16] A study on various reactions of this new nucleophile is now underway.[17]

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