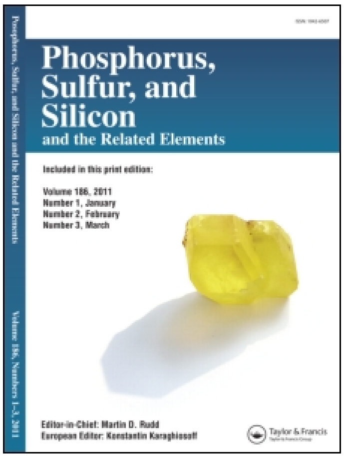

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# REACTION OF 4-CHLORONITROBENZENE WITH ELEMENTAL SULFUR IN LIQUID AMMONIA

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# REACTION OF 4-CHLORONITROBENZENE WITH ELEMENTAL SULFUR IN LIQUID AMMONIA

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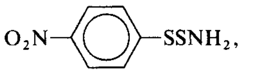
An interesting compound, 4-nitrobenzenethiosulfenamide (**2**),



was isolated in the reaction of 4-chloronitrobenzene (**1**) with elemental sulfur in liquid ammonia at about 20°C. This compound yielded 4-nitrobenzenethiol (**3**), 4-nitroaniline (**4**), 4,4′-dinitrodiphenyl disulfide (**5**) and 4,4′-dinitrodiphenyl sulfide (**6**) upon further reaction in liquid ammonia. When elemental sulfur is dissolved in liquid ammonia, new nucleophile species such as $H_2NS^-NH_4^+$ or $H_2NSS^-NH_4^+$ appear to be formed and to participate in the aromatic nucleophilic reactions. These new nucleophiles, $H_2NS^-NH_4^+$ and $H_2NSS^-NH_4^+$, would undoubtedly participate in the reactions of 4,4′-dinitrodiphenyl disulfide (**5**) and 4,4′-dinitrodiphenyl sulfide (**6**) with elemental sulfur in liquid ammonia, respectively.

## INTRODUCTION

There are numerous investigations on the reactions of organic substances with elemental sulfur[1–3] and also on the cleavage[4–7] of the sulfur linkage of elemental sulfur with various nucleophiles. Among these, amines have been used in the reaction of elemental sulfur with organic substances in a few interesting reactions.[1,8] One useful reaction is the Willgerodt reaction.[9,10] However, the role of elemental sulfur in this amine-catalyzed reaction has not been fully understood.

In addition, the solution containing elemental sulfur in liquid ammonia was shown to give free radical ESR signals.[11] This is believed to be due to the solvated electron in the elemental sulfur-liquid ammonia system.[12] Thus it is quite conceivable that a similar electron transfer reaction takes place in the reaction of elemental sulfur in liquid ammonia. Accordingly, nucleophilic substitution reactions with sulfur-containing nucleophiles such as thiols and thioamides would be favored in liquid ammonia. Indeed, a nucleophilic substitution reaction of *o*- or *p*-nitrohalobenzene with sodium hydrogen sulfide was found to take place readily at such a low temperature as 20°C in liquid ammonia.[13]

We found recently that new nucleophiles i.e., thiohydroxylamine, $H_2NS^-NH_4^+$, and dithiohydroxylamine, $H_2NSS^-NH_4^+$, are readily formed upon dissolving elemental sulfur in liquid ammonia and behave as important nucleophiles in the reaction of 4-nitrobenzenesulfenamide with liquid ammonia[14] and in other reactions.[15]

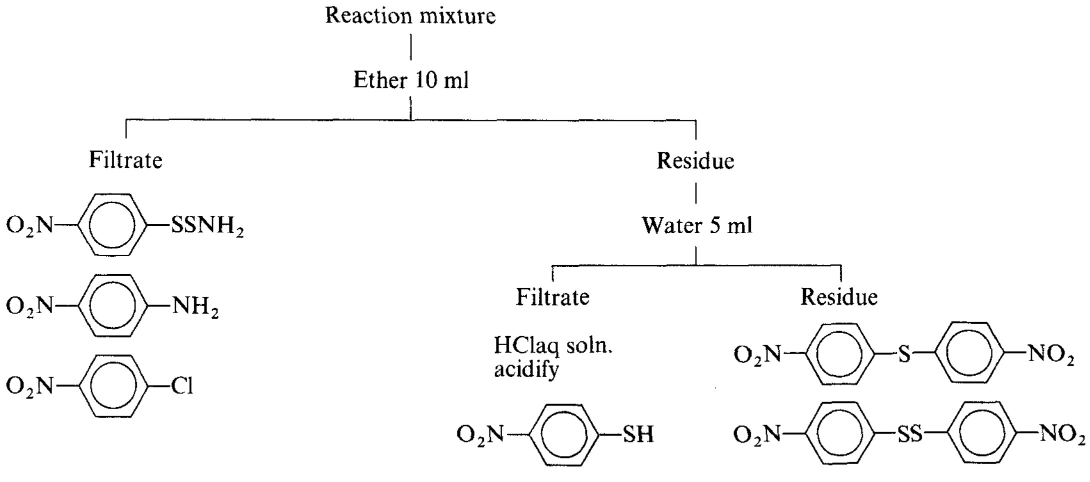
Elemental sulfur dissolved in liquid ammonia dissociates in the following manner:

$$S_8 \xrightleftharpoons{NH_3} H_2N{-}SS_6S^-NH_4^+$$

$$H_2N{-}SS_6S^-NH_4^+ \xrightleftharpoons{NH_3} 2H_2N{-}SS_2S^-NH_4^+$$

$$H_2N{-}SS_2S^-NH_4^+ \xrightleftharpoons{NH_3} 2H_2N{-}SS^-NH_4^+$$

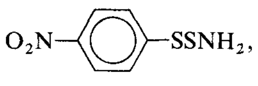
$$H_2N{-}SS^-NH_4^+ \xrightleftharpoons{NH_3} 2H_2N{-}S^-NH_4^+$$



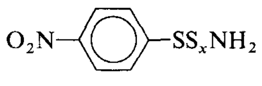
SCHEME I

The generation of thiohydroxylamine was reported by Herlem *et al.*, based upon various measurements.[16]

Both the sulfenyl amide and the thiosulfenyl amide, —$SSNH_2$, are considered to be powerful nucleophiles and expected to replace chloride from 4-chloronitrobenzene (**1**) when formed in situ by dissolving elemental sulfur in liquid ammonia, even at a low temperature, owing mainly to the one-electron transfer reaction. Indeed, 4-chloronitrobenzene (**1**) was found to react with elemental sulfur in liquid ammonia at 20°C to give 4-nitrobenzenethiosulfenamide (**2**),



and 4-nitrobenzenepolythiosulfenamide,



($x$ = 2?), which upon further reaction, were converted to 4-nitroaniline (**4**), 4-nitrobenzenethiol (**3**), 4,4′-dinitrodiphenyl disulfide (**5**) and 4,4′-dinitrodiphenyl sulfide (**6**). This paper deals with the reaction of 4-chloronitrobenzene (**1**) with elemental sulfur in liquid ammonia in connection with our previous work on the reaction of 4,4′-dinitrodiphenyl disulfide (**5**) with liquid ammonia involving the formation of the proposed hypothetical sulfonium intermediate.[14]

## EXPERIMENTAL

### *Material*

*Elemental sulfur.* Commercial powder sulfur was recrystallyzed from carbon disulfide.

*Liquid ammonia.* Commercial liquid ammonia was distilled before use.

*Reaction vessel.* All-titanium autoclave was used for the reaction.

*Reaction of 4-chloronitrobenzene* (**1**) *with elemental sulfur in liquid ammonia.* 4-Chloronitrobenzene (**1**) 0.78 g (5 mmol) and 0.16 g of elemental sulfur were placed in the titanium autoclave. After the autoclave was evacuated, 20 ml. of liquid ammonia was charged into the autoclave which was heated with stirring. The reaction mixtures were separated according to the Scheme I above.

Products were identified by comparison with authentic samples. The yield of each product was determined by the nmr intensity of the aromatic proton at the 2-position. 4-Nitrobenzenethiosulfenamide (**2**) had already been characterized in our earlier work.[14,15]

*Reaction of 4,4′-dinitrodiphenyl disulfide* (**5**) *and 4,4′-dinitrodiphenyl sulfide* (**6**) *with elemental sulfur in liquid ammonia.* 4,4′-Dinitrodiphenyl disulfide (**5**) or 4,4′-dinitrodiphenyl sulfide (**6**), 2.5 mmol, and 80 mg of elemental sulfur were placed in the titanium autoclave and then were allowed to react in the same manner as in the reaction of 4-chloronitrobenzene (**1**) with elemental sulfur in liquid ammonia. The separation of the reaction mixtures was also carried out according to the Scheme I.

## RESULTS AND DISCUSSION

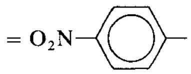
4-Chloronitrobenzene (**1**) reacted with elemental sulfur in liquid ammonia at 20°C to give 4-nitrobenzenepolythiosulfenamide, 4-nitrobenzenethiol

TABLE I

Reaction of 4-chloronitrobenzene (1) with elemental sulfur in liquid ammonia[a]

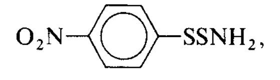
| Run | Temp. (°C) | Time (h) | Yield of products (%)[b] | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | R—SSNH$_2$ | R—NH$_2$ | R—SH | R—SS—R | R—S—R | R—Cl[c] |
| 1 | 20 | 2 | 2 | trace | 10 | 4 | — | 80 |
| 2 | 20 | 4 | 3 | 2 | 10 | 7 | — | 75 |
| 3 | 40 | 2 | 3 | trace | 6 | 10 | — | 78 |
| 4 | 40 | 4 | trace | 2 | 3 | 18 | 10 | 65 |
| 5 | 40 | 6 | trace | 6 | — | 23 | 17 | 46 |
| 6 | 60 | 2 | trace | 23 | — | 16 | 27 | 32 |
| 7 | 60 | 4 | — | 42 | — | 20 | 36 | trace |
| 8 | 60 | 6 | — | 61 | 1 | 8 | 29 | — |
| 9 | 80 | 2 | — | 73 | 12 | 2 | 13 | — |
| 10 | 80 | 4 | — | 78 | 21 | trace | — | — |
| 11 | 80 | 6 | — | 78 | 22 | — | — | — |
| 12 | 100 | 2 | — | 71 | 13 | 7 | — | — |
| 13 | 100 | 4 | — | 78 | 22 | — | — | — |

[a] Substrate: 5 mmol, Elemental sulfur: 0.16 g, Liquid ammonia: 20 ml.

[b] R =


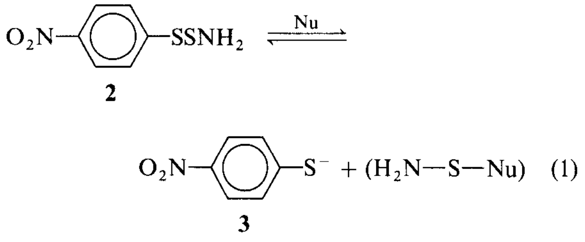
[c] % of recovery.

(3), 4,4′-dinitrodiphenyl disulfide (5) and 4,4′-dinitrodiphenyl sulfide (6) besides 4-nitrobenzenethiosulfenamide (2), an interesting compound that had already been characterized.[14,15] The results are summarized in Table I. The formation of a new species, the thiosulfenamide (2)

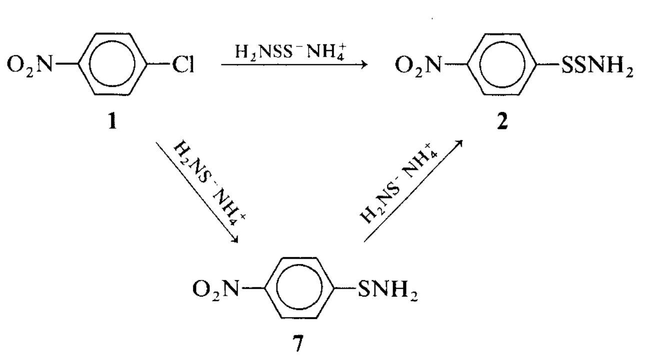


in the reaction with elemental sulfur in liquid ammonia solution is rather interesting since it suggests that elemental sulfur in liquid ammonia can generate such nucleophilic reagents as $H_2NS^-NH_4^+$ and $H_2NSS^-NH_4^+$ which can undergo nucleophilic substitution reactions with 4-chloronitrobenzene (1) as shown below.

The low yield of the thiosulfenamide (2) and the relatively high yield of the thiol (3) in run 1 of the Table I are due to the reaction of the thiosulfenamide (2) with a nucleophile such as thiohydroxylamine or ammonia as shown below.



Nucleophile: $H_2NS^-NH_4^+$, $H_2NSS^-NH_4^+$ or $NH_3$



SCHEME II

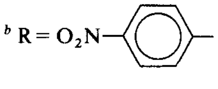
TABLE II

Reaction of 4,4′-dinitrodiphenyl disulfide[5] with elemental sulfur in liquid ammonia[a]

| Run | Time (h) | Yield of product (%)[b] | | | |
|---|---|---|---|---|---|
| | | $R{-}SSNH_2$ | $R{-}SH$ | $R{-}NH_2$ | $R{-}SS{-}R$ |
| 1 | 1 | 4 | 34 | 8 | 58 |
| 2 | 2 | 6 | 43 | 10 | 52 |
| 3 | 4 | 5 | 47 | 11 | 48 |
| 4 | 6 | 6 | 42 | 11 | 55 |

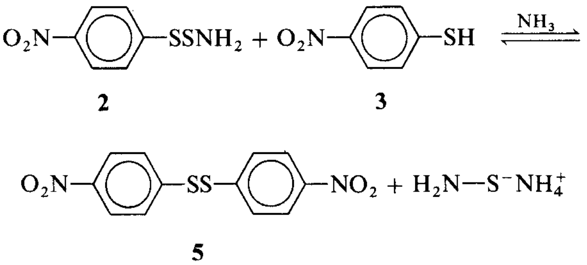
[a] Substrate: 2.5 mmol, Elemental sulfur: 80 mg, Liquid ammonia: 20 ml

[b] R =



This is quite reasonable since 4-nitrobenzenethiolate is a good leaving group. Accordingly, the 4-nitrobenzenethiosulfenamide (**2**) was a minor product and 4-nitrobenzenethiol (**3**) was the major product in this system.

4,4′-Dinitrodiphenyl disulfide (**5**) was undoubtedly formed by the reaction of 4-nitrobenzenethiosulfenamide (**2**) with 4-nitrobenzenethiol (**3**) as shown below.



(2)

This equilibrium was actually confirmed by the reaction of 4,4′-dinitrodiphenyl disulfide (**5**) with elemental sulfur in liquid ammonia at 20°C and the results are summarized in the Table II.

In the presence of a large amount of thiohydroxylamine, $H_2NS^-NH_4^+$, the yield of each product remained nearly constant. (see runs 1–4 in Table II).

A few characteristic features of results in Table I may be the following:

1) As the reaction temperature was raised, the yield of the thiosulfenamide (**2**) decreased.

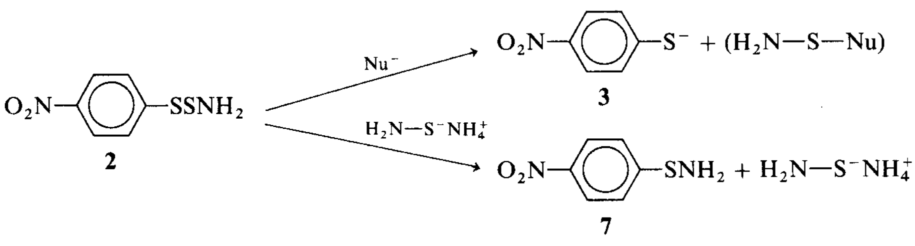
2) Even at a low reaction temperature, formation of 4-nitroaniline (**4**) was observed.

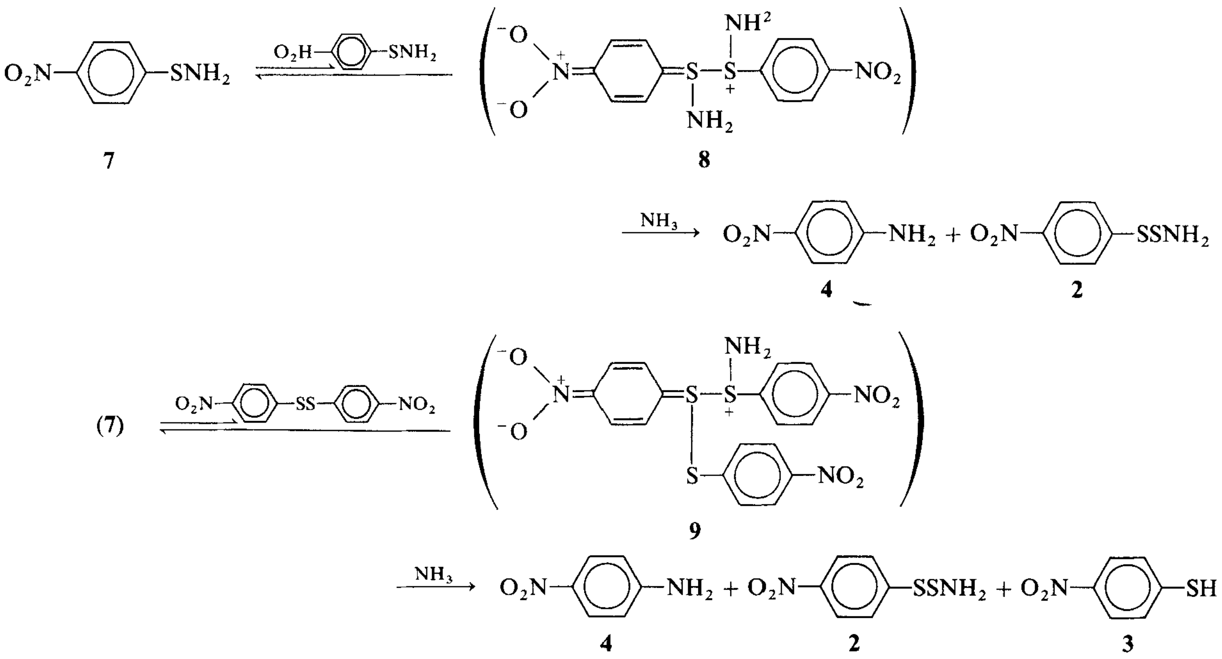
3) As the reaction temperature was raised, the yield of the thiol (**3**) decreased and then increased again.

4) With the increases of both reaction temperature and of reaction time, the yield of 4,4′-dinitrodiphenyl disulfide (**5**) increased and then decreased.

5) 4,4′-Dinitrodiphenyl sulfide (**6**), which had been formed, disappeared as the reaction temperature as well as the reaction time increased.

Apparently the thiosulfenamide (**2**) was readily attacked by nucleophiles such as ammonia and thiohydroxylamine to give the thiol (**3**) and 4-nitrobenzenesulfenamide (**8**) which yield 4,4′-dinitrodiphenyl disulfide (**5**) and 4-nitroaniline (**4**), respectively, in further reactions.

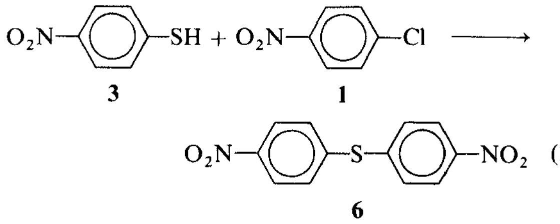




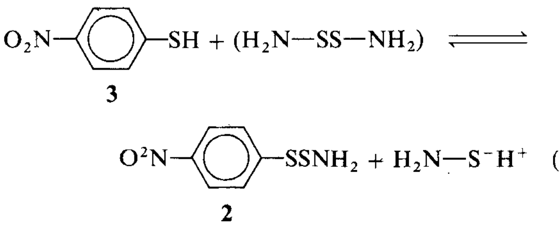
SCHEME III

The formation of 4-nitroaniline (**4**) from 4-nitrobenzenesulfenamide (**7**) can again be interpreted through the incipient formation of the sulfonium intermediate (**8**) or (**9**) shown in Scheme III.[14,15]

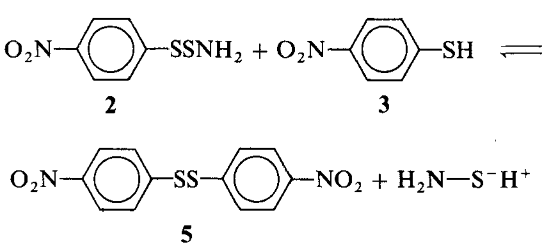
The thiol (**3**) is considered to be the result of the reaction of 4-nitrobenzenethiosulfenamide (**2**) with nucleophiles as depicted in Eq. (1). The decrease (runs 1–4) of the yield of the thiol (**3**) with the increase of reaction temperature must be due to the following further reactions of the thiols (**3**).



(3)



(4)

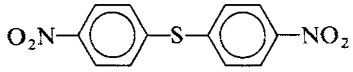


(5)

The increase (runs 8–13) of the thiol (**3**) in the later stages of the reaction would be the result of the reverse reaction of Eq. (5) and the reaction of the sulfenamide (**7**) with the disulfide (**5**) to give 4-nitroaniline (**4**) as shown in Scheme III. It is interesting to note that the thiol (**3**) was consistently obtained in a maximum yield of 22%, whereas the aniline (**4**) was obtained in a maximum final yield of 78%.

The increased formation of the disulfide (**5**) in the presence of the thiol (**3**) would be due to the reactions shown by Eq. (2) and (5). However, the formation of the disulfide (**5**) should be reduced due to the formation of the aniline (**4**) in Scheme III.

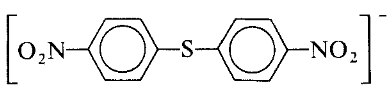
4,4′-Dinitrodiphenyl sulfide (**6**),



once formed according to Eq. (3), decreased as the reaction progressed (see runs 7–13 in Table I), implying that the sulfide (**6**) reacts with some nucleophilic reagent (Eq. 6).

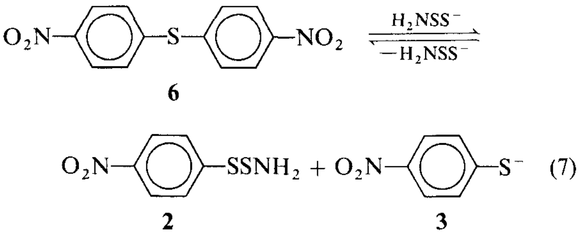
$$\mathrm{R{-}S{-}R} \xrightarrow{\mathrm{Nu}} \mathrm{R{-}Nu} + \mathrm{R{-}S^-} \tag{6}$$

This appears to be a rather strange reaction; however, there is a possibility that the nucleophilic substitution accompanies a one-electron transfer, especially in the reaction of 4,4′-dinitrodiphenyl sulfide (**6**) with elemental sulfur in liquid ammonia, since the sulfide (**6**) is a good electron trap and could readily form the anion radical (**10**).[17] The solution of elemental sulfur in liquid ammonia is known to generate a free radical.[12] Without elemental sulfur, the sulfide (**6**) did not react with liquid ammonia at all under the conditions in Table I.[18] We have carried out the reaction of the 4,4′-dinitrodiphenyl sulfide (**6**) with elemental sulfur in liquid ammonia and indeed obtained 4-nitrobenzenethiosulfenamide (**2**) and 4-nitrobenzenethiol (**3**) together with other identical products formed in the reaction of 4-chloronitrobenzene (**1**) or 4,4′-dinitrodiphenyl disulfide (**5**) with elemental sulfur in liquid ammonia as shown in the Tables I and II. These results are shown in the Table III.



**10**

Thus 4,4′-dinitrodiphenyl sulfide (**6**) did react readily with elemental sulfur in liquid ammonia to give 4-nitrobenzenethiosulfenamide (**2**) and 4-nitrobenzenethiol (**3**) at a relatively low temperature such as 20°C (see runs 1–2 in the Table III). 4-Nitrobenzenethiosulfenamide (**2**) was obviously formed by the nucleophilic substitution of the sulfide (**6**) with dithiohydroxylamine, $H_2NSS^-NH_4^+$, as shown below.



(7)

The formation of 4,4′-dinitrodiphenyl disulfide (**5**) and 4-nitroaniline (**4**) in the further reactions can be explained by a mechanism similar to that of the reaction of 4-chloronitrobenzene (**1**) with elemental sulfur in liquid ammonia.

Thus the decrease of 4,4′-dinitrodiphenyl sulfide (**6**) shown in Table I (runs 6–10) can be explained nicely by the reaction with elemental sulfur in liquid ammonia.

Ultimately, 4-nitroaniline (**4**) and 4-nitrobenzenethiol (**3**) were obtained in maximum yields of 78 and 22%, respectively, in this reaction (runs 11 and 13 in Table I).

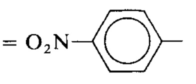
TABLE III

Reaction of 4,4′-dinitrodiphenyl sulfide[6] elemental sulfur in liquid ammonia[a]

| Run | Temp. (°C) | Time (h) | Yield of product (%)[b] | | | |
|---|---|---|---|---|---|---|
| | | | R—SH | R—SSNH$_2$ | R—SS—R | R—NH$_2$ |
| 1 | 0 | 4 | 2 | trace | 1 | — |
| 2 | 20 | 6 | 6 | 3 | 10 | — |
| 3 | 40 | 2 | 8 | 4 | 13 | — |
| 4 | 40 | 4 | 10 | 4 | 18 | trace |
| 5 | 40 | 6 | 12 | 4 | 22 | 1 |
| 6 | 60 | 2 | 17 | — | 28 | 7 |
| 7 | 60 | 4 | 25 | — | 28 | 20 |
| 8 | 60 | 6 | 37 | — | 24 | 25 |

[a] Substrate: 2.5 mmol, Elemental sulfur: 80 mg, Liquid ammonia: 20 ml

[b] R =



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18. 4,4′-Dinitrodiphenyl sulfide (6) reacted with liquid ammonia only after 4 h at 120°C to give 4-nitroaniline (4), 0.3%, and 4,4′-dinitrodiphenyl disulfide (5), 0.3%, respectively.