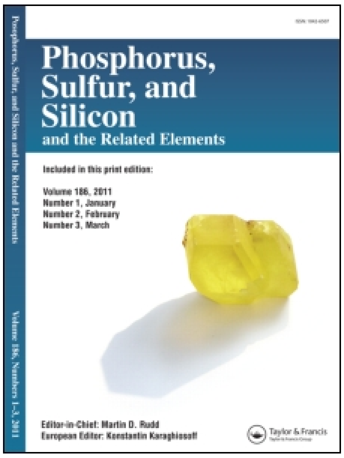

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REACTION OF AROMATIC NITRO COMPOUNDS WITH ELEMENTAL SULFUR IN LIQUID AMMONIA AND AMINES

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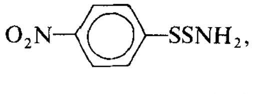
Aromatic nitro compounds were reduced with elemental sulfur in liquid ammonia and in amines, yielding the corresponding anilines. However, introduction of a substituent on the benzene ring or variation of the amine changed somewhat the pattern of this reaction. For example, 4-nitrotoluene (**3**) and 4-cyanonitrobenzene (**6**) were found to give not only the corresponding reduced products but also 4,4′-dicyanodiphenyl disulfide (**10**), formed by replacement of the nitro group, in addition to 4-cyanoaniline (**9**) in the reaction with elemental sulfur in liquid ammonia. Probable mechanisms of these reactions are discussed in the light of new knowledge on the similar reactions of elemental sulfur.

INTRODUCTION

Elemental sulfur in liquid ammonia and amines was found to show rather interesting physical and chemical properties.[1,2] For example, elemental sulfur is dissociated to form powerful nucleophiles, $H_2NS^-NH_4^+$ or $H_2NSS^-NH_4^+$, in both liquid ammonia and amines, often giving free radical ESR signals.[3] One of the interesting reactions of elemental sulfur in amines is the Willgerodt Reaction[4]; however, its mechanism and the role of elemental sulfur have not been thoroughly understood.

Our earlier study[5] indicated that elemental sulfur in liquid ammonia would generate new powerful nucleophilic species, e.g., thiohydroxylamine, $H_2NS^-NH_4^+$, and dithiohydroxylamine, $H_2NSS^-NH_4^+$, which appear to react readily with 4-chloronitrobenzene to yield interesting products such as 4-nitrobenzenethiosulfenamide,



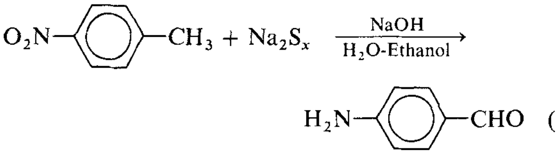
and others at a relatively low temperature such as 20°C.[6] The elemental sulfur is believed to dissociate in liquid ammonia according to the following equations.

$$S_8 \overset{NH_3}{\rightleftharpoons} H_2NSS_6S^-NH_4^+ \overset{NH_3}{\rightleftharpoons} 2H_2NSS_2S^-NH_4^+ \overset{NH_3}{\rightleftharpoons} 4H_2NSS^-NH_4^+ \overset{NH_3}{\rightleftharpoons} 8H_2NS^-NH_4^+$$

Furthermore, elemental sulfur in liquid ammonia is expected to reduce nitro, azo, azoxy groups, disulfides and quinones, respectively,[8] like ammonium or sodium sulfides and sodium hydrosulfite.

As for the reductions of aromatic nitro compounds with reducing systems containing sulfur, there have been a number of investigations since the turn of the century. For instance, Blanksma reported that nitrobenzene was reduced to aniline with sodium disulfide in ethanol in 78% yield.[9] Lapworth *et al.* observed, however, that reduction of 4-chloronitrobenzene with sodium disulfide and calcium chloride in water gave 4-chlorophenylhydroxylamine (68%).[10] Willstätter *et al.* also reported the formation of phenylhydroxylamine (83%) in the reduction of nitrobenzene with hydrogen sulfide and ammonia in ethanol.[11]

Blanksma also confirmed the reduction of 4-nitrotoluene with sodium disulfide and calcium chloride in water to give 4-methylphenylhydroxylamine (53%).[9] One interesting reaction is the formation of 4-aminobenzaldehyde by treatment of 4-nitrotoluene with sodium polysulfide and sodium hydroxide in water and ethanol.[12] The reaction involves simultaneous reduction of nitro group and oxidation of the methyl group (Eq. 1).



(1)

All these reactions seem to indicate that sulfur plays an important role in the reduction of the nitro group.

We found that simple aromatic nitro compounds such as nitrobenzene (**5**) and 4-cyanonitrobenzene (**6**) were readily reduced with elemental sulfur both in liquid ammonia and in some amines to yield the corresponding anilines.

However, 4-nitrotoluene (**3**) was found to react with elemental sulfur in liquid ammonia yielding toluidine (**7**), 4-cyanoaniline (**9**) and 4,4′-dicyanodiphenyl disulfide (**10**). 4-Cyanonitrobenzene (**6**) was also found to react with elemental sulfur in liquid ammonia, affording 4-cyanoaniline (**9**) and 4,4′-dicyanodiphenyl disulfide (**10**). We now wish to report these reductions and some related reactions.

EXPERIMENTAL

Materials

Substituted nitrobenzenes (**1**)–(**5**): The commerically available products were used for the reaction after recrystallization and distillation, respectively.

4-Cyanonitrobenzene (**6**): 4-Cyanonitrobenzene (**6**) was synthesized by treating 4-nitrobenzoic acid with *p*-toluenesulfonamide and phosphorus pentachloride following the method described in literature.[13] White yellow crystals, mp. 148°C, were obtained upon recrystallization from 50% acetic acid.

Elemental sulfur: Commerical powder sulfur was used for the reaction after recrystallization from carbon disulfide.

Liquid ammonia and amines: Commerical ammonia and amines were distilled just before use for the reactions.

Reaction of 4-Nitrotoluene (**3**) *with Elemental Sulfur in Liquid Ammonia*

4-Nitrotoluene (**3**), 1.37 g (10 mmol), and elemental sulfur, 0.32 g, were placed into an all-titanium autoclave. After the autoclave was evacuated, 20 ml of liquid ammonia was charged into the autoclave, and the mixture was allowed to react with vigorous stirring for 6 h at 100°C. Then ammonia was evaporated and the reddish-brown residual mixture was extracted with 30 ml of ether. The ethereal solution was extracted with 20 ml of aqueous 10% hydrogen chloride solution, and 4,4′-dicyanodiphenyl disulfide (**10**) and 4-nitrotoluene (**3**) were obtained from the ether layer. Toluidine (**7**) and 4-cyanoaniline (**9**) were obtained from the aqueous layer by extraction with ether after the aqueous solution was made alkaline. Yields of all these products were determined by measuring the nmr intensities of aromatic and methyl protons. These products were identified separately upon comparison with the respective samples.

Reaction of 4-Nitrotoluene (**3**) *with Elemental Sulfur in Amines*

A typical run was carried out as follows. 4-Nitrotoluene (**3**), 1.37 g (10 mmol), elemental sulfur, 0.32 g, and 20 ml of respective amine were placed into an all-titanium autoclave (50 ml capacity) and then the mixture was allowed to react for 6 h at 100°C. The reaction mixture was treated in a similar manner as in the reaction of 4-nitrotoluene (**3**) with elemental sulfur in liquid ammonia. In this reaction, however the only product obtained was toluidine (**7**) and its yield was determined by glpc.

Reaction of Nitrobenzene (**5**) *with Elemental Sulfur in Liquid Ammonia and Amines*

A typical run was carried out as follows. Nitrobenzene (**5**), 1.23 g (10 mmol), and elemental sulfur, 0.32 g, were placed into an all-titanium autoclave (50 ml capacity) and then liquid ammonia or amines was charged. After allowing the mixture to react, ammonia or amine was evaporated and aniline (**8**) was extracted with ether from the reaction mixture. The yield was determined by glpc.

Reaction of 4-Cyanonitrobenzene (**6**) *with Elemental Sulfur in Liquid Ammonia*

4-Cyanonitrobenzene (**6**), 1.48 g (10 mmol), and elemental sulfur, 0.32 g, were placed into an all-titanium autoclave (50 ml capacity). After the autoclave was evacuated, liquid ammonia, 20 ml was charged and then the mixture was allowed to react for 6 h at 100°C. 4-Cyanoaniline (**9**) and 4,4′-dicyanodiphenyl disulfide (**10**) were obtained by extraction of the reaction mixture with 30 ml of ether, after evaporation of ammonia. 4-Cyanoaniline (**9**) was obtained by initial treatment of the ether layer with aqueous hydrogen chloride (10%) and subsequent neutralization.

Reaction of 4-Cyanonitrobenzene (**6**) *with Elemental Sulfur in Amines*

A typical run was carried out in a similar manner to the reaction of nitrobenzene (**5**) with elemental sulfur in amines. In this reaction the only product obtained was 4-cyanoaniline (**9**). The yield of 4-cyanoaniline (**9**) was determined by measuring the nmr intensity of the aromatic protons.

Reaction of Substituted Nitrobenzene (**1**)–(**6**) *with Elemental Sulfur in Propylamine*

A typical run was carried out in a similar manner to the reaction of nitrobenzene (**5**) with elemental sulfur in amines. In these reactions the products obtained were substituted anilines. The yields of substituted anilines were determined by glpc and by measuring the nmr intensities of aromatic and methyl protons (see Table IV).

Spectroscopic Data of Substrates and Products

4-Nitrophenol (**1**): NMR(CD_3OD) $\delta = 6.88$ (2H, d, J = 9.0 Hz, aromatic) and 8.17 (2H, d, J = 9.0 Hz, aromatic).

4-Methoxynitrobenzene (**2**): NMR($CDCl_3$) $\delta = 3.87$ (3H, s, OCH_3), 6.94 (2H, d, J = 9.0 Hz, aromatic) and 8.15 (2H, d J = 9.0 Hz, aromatic).

4-Methoxyaniline: NMR($CDCl_3$) $\delta = 3.72$ (3H, s, OCH_3), 4.90 (2H, m, NH_2) and 6.70 (4H, s, aromatic).

4-Nitrotoluene (**3**): NMR($CDCl_3$) $\delta = 2.44$ (3H, s, CH_3), 7.36 (2H, d, J = 8.0 Hz, aromatic) and 8.13 (2H, d, J = 8.0 Hz, aromatic).

4-Cyanonitrobenzene (**6**): NMR($CDCl_3$) $\delta = 7.93$ (2H, d, J = 8.4 Hz, aromatic) and 8.41 (2H, d, J = 8.4 Hz, aromatic).

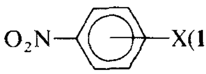
Toluidine (**7**): NMR($CDCl_3$) $\delta = 2.18$ (3H, s, CH_3), 3.40 (2H, s, NH_2) and 6.55 (2H, d, J = 8.0 Hz, aromatic) and 6.95 (2H, d, J = 8.0 Hz, aromatic).

4-Cyanoaniline(**9**): NMR($CDCl_3$)$\delta = 4.18$(2H, broad, NH_2), 6.64 (2H, d, J = 8.4 Hz, aromatic) and 7.38 (2H, d, J = 8.4 Hz, aromatic). (mp. 86°C from ethanol).

4,4′-Dicyanodiphenyl Disulfide (**10**): IR(KBr) 2210 (CN) cm^{-1}. NMR($CDCl_3$) $\delta = 7.54$ (10H, s, aromatic). MS (70 eV), m/e, M^+, 268. (mp. 169°C from chloroform). Found S, 23.5%, Calcd. S, 23.8%.

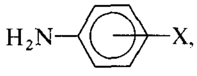
RESULTS AND DISCUSSION

When substituted nitrobenzenes,



(**1–6**)

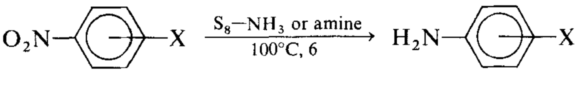
were treated with elemental sulfur in liquid ammonia or amines (propyl- and butylamines, morpholine and piperidine) at 100°C, the nitro group was reduced and the corresponding substituted anilines,



were obtained in some cases in excellent yields. The results are summarized in Tables I–IV (100°C, 6 h) together with the pKa values of the amines used.

In the reaction of nitrobenzenes with elemental sulfur in such tertiary amines as triethylamine, however, no reaction product was obtained.

As shown in Tables I–IV, the aromatic nitro group was reduced to an amino group with elemental sulfur not only in liquid ammonia but also in such primary amines as propylamine and butylamine and even in such secondary amines as diethylamine, morpholine and piperidine (Eq. 2).



(X = 4-OCH_3, -CH_3, -CN) (2)
3-Cl and H

The yield of aniline was found to be quite high when the reaction was carried out in primary amines, whereas, in the reduction with elemental sulfur in secondary amines the yield of aniline was low (see Tables I–III). This seems to imply that the hydrogen atom of the amino group of the aniline originated from the thiohydroxylamine or dithiohydroxylamine, which in turn was oxidized to afford R—NH—S—NH—R, R—N=S=N—R or S_4N_4 (when ammonia was used).[1] A few years ago Sasaki and Olsen reported that the reaction of benzylamine with elemental sulfur afforded benzyliden benzylimide (Schiff base), together with hydrogen sulfide and ammonia.[14] In our reduction,

TABLE I

Reduction of 4-nitrotoluene (**3**) with elemental sulfur in liquid ammonia and amines[a]

Run	Amine	pKa	Yield of Toluidine (**7**) (%)
1	Ammonia	9.21	22[b]
2	Propylamine	10.53	96
3	Butylamine	10.43	40
4	Diethylamine	10.98	8
5	Morpholine	8.36	5
6	Piperidine	11.22	14

[a] 4-Nitrotoluene (**3**): 1.37 g (10 mmol), Elemental sulfur: 0.32 g, Liquid ammonia and amines: 20 ml, React. temp.: 100°C, React. time: 6 h.

[b] Other products were also obtained.

TABLE II

Reduction of nitrobenzene (**5**) with elemental sulfur in liquid ammonia and amines[a]

Run	Amine	pKa	Yield of aniline (**8**)
1	Ammonia	9.21	trace
2	Propylamine	10.53	100
3	Butylamine	10.43	31
4	Diethylamine	10.98	5
5	Morpholine	8.36	11
6	Piperidine	11.22	12

[a] Nitrobenzene (**5**): 1.23 g (10 mmol), Elemental sulfur: 0.32 g, Liquid ammonia and amine: 20 ml, React temp.: 100°C, React time: 6 h.

TABLE III

Reduction of 4-cyanonitrobenzene (**6**) with elemental sulfur in liquid ammonia and amines[a]

Run	Amine	pKa	Yield of 4-cyanoaniline (**9**)
1	Ammonia	9.21	41[b]
2	Propylamine	10.53	100
3	Butylamine	10.43	100
4	Diethylamine	10.98	58
5	Morpholine	8.36	22
6	Piperidine	11.22	66

[a] 4-Cyanonitrobenzene (**6**): 1.48 g (10 mmol), Elemental sulfur: 0.32 g, Liquid ammonia and amine: 20 ml, React temp.: 100°C, React. time: 6 h.

[b] Other products were also obtained.

TABLE IV

Reduction of substituted nitrobenzenes with elemental sulfur in propylamine[a]

Run	Substrate	Yield of substituted aniline (%)
1	4-Nitrophenol (**1**)	0
1	4-Methoxynitrobenzene (**2**)	42
3	4-Methylnitrobenzene (**3**)	96
4	3-Chloronitrobenzene (**4**)	95
5	Nitrobenzene (**5**)	100
6	4-Cyanonitrobenzene (**6**)	100

[a] Substrate: 10 mmol, Elemental sulfur: 0.32 g, Propylamine: 20 ml React. temp.: 100°C, React. time: 6 h.

the high yield of aniline obtained by the reaction with such a primary amine as propylamine is also considered to be the result of the formation of the corresponding Schiff base, i.e.,

$CH_3CH_2{-}CH{=}N{-}CH_2CH_2CH_3$.

Thus, it is quite understandable that the yield of the aniline was low when secondary amines were used and aniline was not obtained when a tertiary amine such as triethylamine was used. In the reaction of nitrobenzenes in propylamine, except for the case of 4-nitrophenol (**1**) and 4-methoxynitrobenzene (**2**), the corresponding anilines were obtained quantitatively (see Table IV).

The yield of the 4-cyanoaniline (**9**) in the reduction of 4-cyanonitrobenzene (**6**) was relatively higher than those of aniline derivatives from 4-methoxynitrobenzene (**2**), 4-nitrotoluene (**3**) and nitrobenzene (**5**) (see Tables I–III and IV). Apparently the electron-withdrawing group facilitates the reduction of nitro group. Perhaps the electron-withdrawing substituent facilitates the formation of a nitroaromatic radical anion by one-electron transfer from the thio- or dithiohydroxylamine species.[15]

4-Nitrophenol (**1**) did not react at all with elemental sulfur, even in propylamine, and in the case of 4-methoxynitrobenzene (**2**) the yield of 4-methoxyaniline was relatively low, 42% (see runs 1 and 2 in Table IV), probably because both hydroxy and methoxy groups are highly electron-releasing.

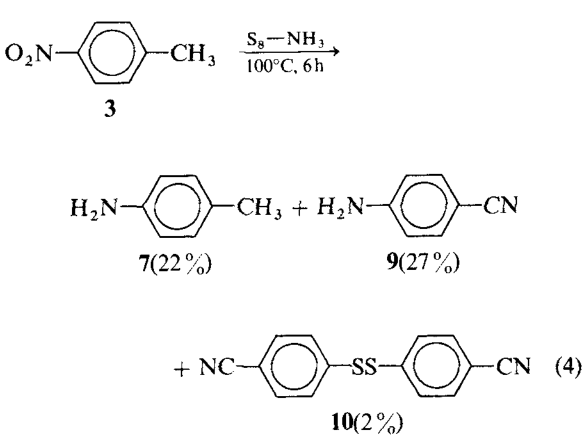
Inspection of the data in Tables I–III reveals that the yield of aniline is higher with an amine of higher basicity, probably owing to the facile dissociation of N-alkylthiohydroxylamine, R—NH—SH, with a more basic amine (Eq. 3). This, in turn, would

$$R{-}NH{-}SH \xrightleftharpoons{R-NH_2} R{-}NH{-}S^- + R{-}NH_3^+ \qquad (3)$$

facilitate the electron transfer from the sulfur atom to the nitro group.

The reactions of both 4-nitrotoluene (**3**) and 4-cyanonitrobenzene (**6**) with elemental sulfur in liquid ammonia are different from those in amines. When 4-nitrotoluene (**3**) was treated with elemental sulfur in liquid ammonia at 100°C for 6 h, two products, 4-cyanoaniline (**9**), 27%, and 4,4′-dicyanodiphenyl disulfide (**10**), 2%, were obtained besides toluidine (**7**), 22%. Obviously, the methyl group was converted to a cyano group during the reaction and the formation of 4,4′-dicyanodiphenyl disulfide (**10**) implies the replacement of the nitro group by a sulfenyl nucleophile (Eq. 4).

The formation of 4-cyanoaniline (**9**) is interesting since both the reduction of nitro group and the ammono-oxidation of the methyl group are taking place simultaneously.

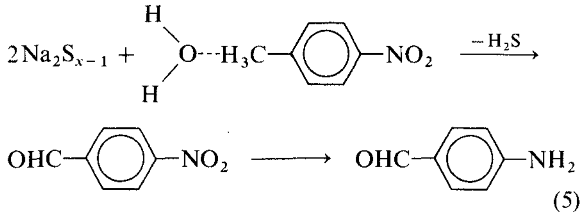


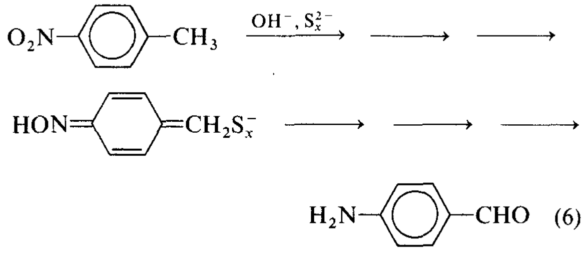
3

7(22%) **9**(27%)

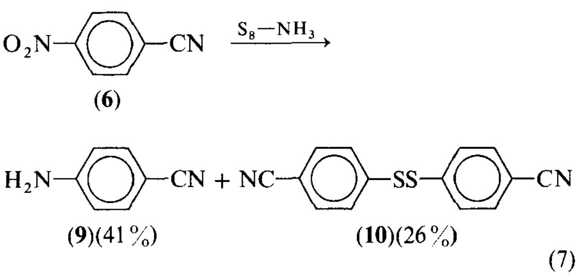
10(2%) (4)

Earlier, Blanksma reported that 4-nitrotoluene (**3**) was found to react with sodium sulfide or sodium polysulfide affording 4-aminobenzaldehyde[12] and Beard *et al.* later proposed the following mechanism for this reaction[16] (Eq. 5). Shchukina also reported a similar mechanism involving a polynitron intermediate.[17] Recently, Ogata *et al.* proposed the following mechanism which involves the simultaneous reduction of the nitro group and the oxidation of the methyl group (Eq. 6).


(5)


(6)

When 4-cyanonitrobenzene (**6**) was treated with elemental sulfur in liquid ammonia, both 4-cyanoaniline (**9**) and 4,4′-dicyanodiphenyl disulfide (**10**) were also obtained (Eq. 7).


(**6**)

(**9**)(41%) (**10**)(26%)

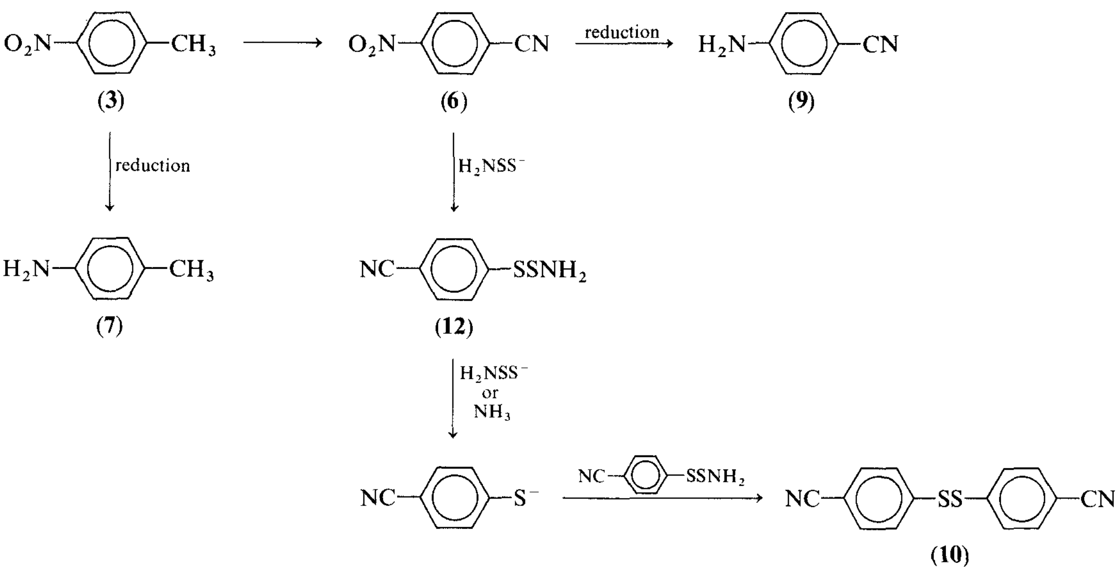
(7)

The probable pathway of the reaction is illustrated in scheme I below.

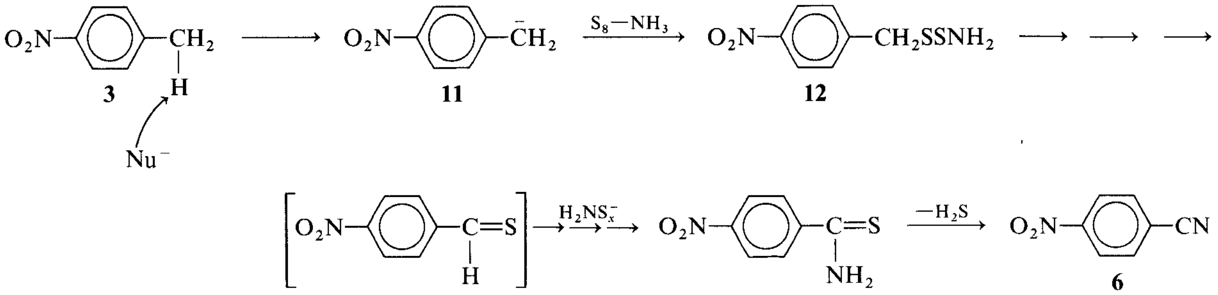
4,4′-Dicyanodiphenyl disulfide (**10**) is considered to be formed according to scheme I which was proposed by us previously.[5] In the reaction of the 4-nitrotoluene (**3**) with elemental sulfur in liquid ammonia to form the 4,4′-dicyanodiphenyl disulfide (**10**), the initial step would be the conversion of the methyl group to the cyano group, and in the subsequent step, nucleophilic substitution of the nitro group with elemental sulfur in liquid ammonia would proceed.

It is well known that the nitro group is readily substituted with some strong thiolate nucleophiles such as sodium thiolate.[8]

The probable mechanistic path of the formation of 4-cyanonitrobenzene (**6**) from 4-nitrotoluene (**3**)



SCHEME I



SCHEME II

is illustrated in Scheme II. Owing to the presence of the 4-nitro group, even such weak bases as thiohydroxylamine, $H_2NS^-NH_4^+$, or ammonia would cause partial deprotonation to give carbanion (**11**), which then readily reacts with elemental sulfur in liquid ammonia to give the thiosulfenamide (**12**).

In the reaction with elemental sulfur in primary and secondary amines, however, such products, i.e. 4-cyanonitrobenzene (**6**), 4-cyanoaniline (**9**) and 4,4-dicyanodiphenyl disulfide (**10**) were not obtained.

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