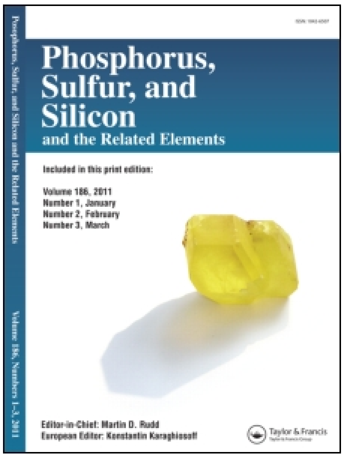

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REDUCTION OF NITROGEN FUNCTIONAL GROUPS WITH ELEMENTAL SULFUR IN LIQUID AMMONIA AND AMINES

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Nitrosobenzene and phenylhydroxylamine were reduced with elemental sulfur in liquid ammonia and amines to give aniline as the major product. Although hydrazobenzene was obtained by the reactions of azoxybenzene and azobenzene with elemental sulfur in liquid ammonia and amines, the expected aniline was not obtained. The utilities of elemental sulfur in liquid ammonia and amines as reductant is discussed.

INTRODUCTION

Recently, we reported the reactions of nitro compounds with elemental sulfur in liquid ammonia and amines affording only aniline in good yields.[1] Since in this reaction no intermediates are observed, the mechanism and the selectivity of reduction by elemental sulfur in liquid ammonia and amines are not fully understood. This stimulated us to investigate the reactions of nitrosobenzene, phenylhydroxylamine, azoxybenzene and azobenzene with elemental sulfur in liquid ammonia and amines in an attempt to extend this reaction to various nitrogen functional groups.

Although there have been numerous reports on the reductions of nitro and related compounds with a variety of reductants e.g., metallic hydrides,[2] metals[3] and sodium sulfides in ethanol,[4] reactions with elemental sulfur, except for our study on the reaction of nitro compounds with elemental sulfur in liquid ammonia and amines,[1] have not been reported.

We now wish to report the reductions of nitrogen functional groups, for example, nitrosobenzene, phenylhydroxylamine, azoxybenzene, azobenzene and hydrazobenzene with elemental sulfur in liquid ammonia and amines.

It is well known that free radicals can be observed in the solutions of elemental sulfur in amines.[5] Thus, the system of elemental sulfur in amines seems to be preferable for the reduction of some organic compounds, e.g., nitro and related compounds, since it can act as an electron donor. We have already reported some reactions of organic compounds with elemental sulfur in liquid ammonia and amines and have shown the utility of elemental sulfur in liquid ammonia and amines for nucleophilic substitutions, oxidations[6] and reductions.[1] Moreover, we reported that a new species, $H_2NSS^-NH_4^+$, was formed (Scheme 1) and plays an important role in the reactions of elemental sulfur in liquid ammonia and amines.[7]

$$S_8 \xrightleftharpoons{NH_3} H_2NSS_6S^-NH_4^+$$

$$H_2NSS_6S^-NH_4^+ \xrightleftharpoons{NH_3} 2\ H_2NSS_2S^-NH_4^+$$

$$H_2NSS_2S^-NH_4^+ \xrightleftharpoons{NH_3} 2\ H_2NSS^-NH_4^+$$

$$H_2NSS^-NH_4^+ \xrightleftharpoons{NH_3} 2\ H_2NS^-NH_4^+$$

SCHEME 1

RESULTS AND DISCUSSION

Nitrobenzenes have been already found to be reduced with elemental sulfur in liquid ammonia and amines giving only anilines. However, since no intermediates were observed, the course of the reactions is still unclear. It is well known that there are various pathways for the reduction of nitrobenzene and related compounds depending on the reductant.

Nitrosobenzene was found to react with elemental sulfur in liquid ammonia and amines to afford aniline and azoxybenzene as major products. These results are shown in Table I.

Aniline was obtained in good yield (60%) by the reaction in liquid ammonia at 40°C. Surprisingly, nitrosobenzene was found to form azoxybenzene in the absence of elemental sulfur in methylamine (run 3).[10] W. Foerst has demonstrated without explanation the formation of azoxybenzene with triphenylphosphine.[11] W. P. Neumann *et al.*, reported on the reactions of nitrobenzene with alkyl tin hydride, Et_3SnH, to give azoxybenzene and azobenzene.[12] Moreover, sodium borane trisulfide, $NaBH_2S_3$, was found to reduce nitrosobenzene to give aniline in good yields.[13] Thus, the products obtained are different depending on the reductant. As mentioned above, it seems that there are two pathways in the reaction of nitrosobenzene with elemental sulfur in liquid ammonia and amines: Path a: the direct formation of aniline, and path b: the formation of azobenzene via azoxybenzene.

TABLE I

Reactions of nitrosobenzene with elemental sulfur in liquid ammonia and methylamine

Run	S_8 (mg-atom)	Amine	Yield of Products (%) Aniline	Azoxybenzene	Azobenzene	Hydrazobenzene
1	3	CH_3NH_2	34	19	12	trace
2	3	NH_3	60	15	2	0
3	0	CH_3NH_2	0	64	0	0

Substrate: 1 mmol, amine: 5 ml, reaction time: 2 h; reaction temperature: 40°C.

TABLE II

Reactions of phenylhydroxylamine with elemental sulfur in liquid ammonia and methylamine

Run	Amine	S_8 (mg-atom)	Reaction Temperature (°C)	Yields of Products (%)			
				Aniline	Azoxybenzene	Azobenzene	Hydrazobenzene
1	CH_3NH_2	3	40	93	4	1	trace
2	CH_3NH_2	3	100	78	3	5	2
3	NH_3	3	40	86	5	trace	0
4	CH_3NH_2	0	40	0	94	0	0

Substrate: 1 mmol, amine: 5 ml, reaction time: 2 h.

Phenylhydroxylamine was also found to react with elemental sulfur in liquid ammonia and amines to form aniline as major product, and also azoxybenzene, azobenzene and hydrazobenzene. These results are summarized in Table II.

These results suggest that phenylhydroxylamine is reduced predominantly to aniline by elemental sulfur in liquid ammonia and amines, and the yields of aniline are not dependent on the reaction temperature (runs 1, 2 and 3). The selectivity of the formation of aniline is rather higher than in the reaction of nitrosobenzene with elemental sulfur in liquid ammonia and amines. Thus, the usefulness of elemental sulfur in liquid ammonia and amines for the reduction of nitrogen functional groups was confirmed by the results in Tables I and II.

Further, we carried out the reaction of azoxybenzene, azobenzene and hydrazobenzene with elemental sulfur in liquid ammonia and amines. Azoxybenzene was found to react with elemental sulfur in liquid ammonia and various amines affording hydrazobenzene. These results are shown in Table III.

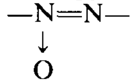
The results in Table III suggest that elemental sulfur in such primary alkylamines as propylamine or butylamine are excellent reductant systems for the azoxy group,  $\underset{\substack{\downarrow \\ O}}{-N{=}N-}$, to the hydrazo group, —NHNH—. Hydrazobenzene especially is obtained in very high yield (80–84%) when propyl- and butylamines are used (runs 4

TABLE III

Reactions of azoxybenzene with elemental sulfur in liquid ammonia and amines

Run	Amine	Reaction Temperature (°C)	Yields of Products (%)	
			Azobenzene	Hydrazobenzene
1	Ammonia	100	53	5
2	Methylamine	100	38	63
3	Methylamine	40	67	36
4	Propylamine	100	8	80
5	Butylamine	100	12	84
6	Allylamine	100	13	58
7	Diethylamine	100	36	11
8	Dipropylamine	100	12	8
9	Triethylamine	100	0	0

Substrate: 1 mmol, elemental sulfur: 3 mg-atom, Amine: 5 ml, reaction time: 2 h.

TABLE IV

Reactions of azobenzene with elemental sulfur in liquid ammonia and amines

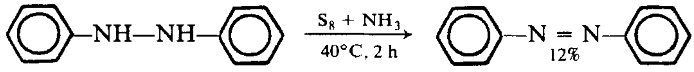
Run	Amine	Reaction Temperature (°C)	Yield of Hydrazobenzene (%)
1	Ammonia	100	trace
2	Methylamine	100	56
3	Methylamine	60	6
4	Propylamine	100	59
5	Piperidine	100	trace
6	Triethylamine	100	0

Substrate: 1 mmol, elemental sulfur: 3 mg-atom, amine: 5 ml, reaction time: 2 h.

and 5). On the other hand, when ammonia was used, azobenzene and hydrazobenzene were obtained in low yield (run 1); also when a secondary amine was used. The use of elemental sulfur in triethylamine is unfavorable for the reduction of azoxybenzene (run 9).

Azobenzene was also treated with elemental sulfur in liquid ammonia and various amines to give hydrazobenzene in moderate yields after rapid separation of the reaction mixtures. The results are summarized in Table IV.

The results show that hydrazobenzene is obtained in high yield when propyl- and butylamines are used. However, in no case was aniline detected. In spite of the high yield of hydrazobenzene by the reaction of azoxybenzene with elemental sulfur in propylamine (run 4 in Table III), hydrazobenzene was obtained in only 59% yield from azobenzene (run 4 in Table IV). These results suggest that there is an equilibrium between azobenzene and hydrazobenzene in the presence of elemental sulfur in amine. The hydrazobenzene was allowed to react with elemental sulfur in liquid ammonia and was found to give azobenzene (eq. 1)



(1)

This fact suggests that elemental sulfur in liquid ammonia reacts with hydrazobenzene as an oxidant rather than as a reductant and that there is an equilibrium between azobenzene and hydrazobenzene. Thus, aniline was not obtained in the reaction of hydrazobenzene with elemental sulfur in liquid ammonia.

The complete system of reactions of nitrobenzene, nitrosobenzene, azoxybenzene and related compounds with elemental sulfur in liquid ammonia and amines is depicted as fig. 1.

EXPERIMENTAL

Materials. Nitrosobenzene and phenylhydroxylamine. Nitrosobenzene and phenylhydroxylamine were synthesized by the literature methods.[8,9] *Azoxybenzene, azobenzene and hydrazobenzene.* Commercial materials were used after recrystallization from alcohol. *Elemental sulfur.* Commercial material was used after recrystallization from carbon disulfide. *Liquid ammonia.* Once-distilled commercial material was used. *Amines.* Commercially available amines were used after two distillations. *Reaction vessel.* An all-titanium autoclave was used in all reactions to avoid corrosion by elemental sulfur in liquid ammonia and amines.

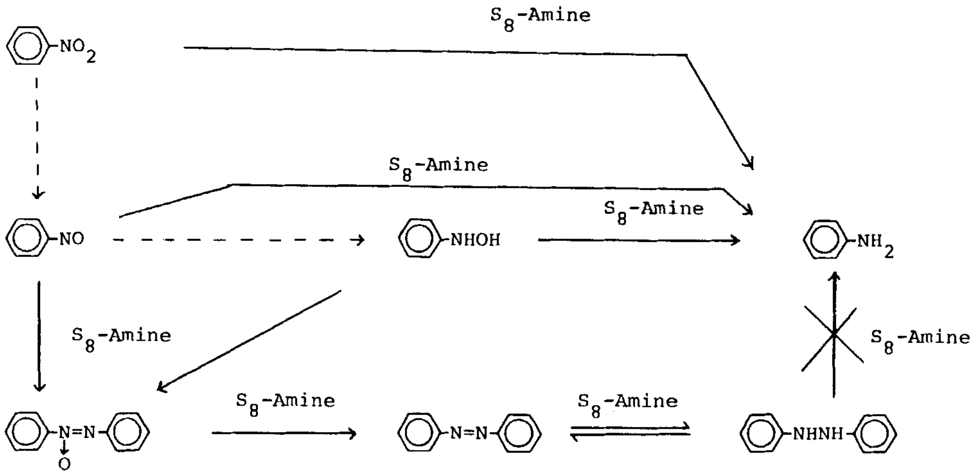


FIGURE 1

Reaction of Nitrosobenzene and Phenylhydroxylamine with Elemental Sulfur in Liquid Ammonia and Amines. 1 Mmol of nitrosobenzene or phenylhydroxylamine and 2 mg-atom of elemental sulfur are placed into the autoclave and, after evacuation, 5 ml of liquid ammonia or amine are charged. Reaction mixtures obtained by evaporation of ammonia or amine were chromatographed on silica gel (Wako gel C-300) using chloroform as eluent. The yields of aniline were determined by G.C.

Reaction of Azoxybenzene, Azobenzene and Hydrazobenzene with Elemental Sulfur in Liquid Ammonia and Amines. Azoxybenzene, Azobenzene or hydrazobenzene (1 mmol) and 2 mg-atom of elemental sulfur are placed in the titanium autoclave. After evacuation, ammonia or amines are charged. Reaction mixtures were separated by column chromatography on silica gel (Wako gel C-300) using a solvent mixture of chloroform and hexane (1 : 1 volume ratio) as eluent.

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