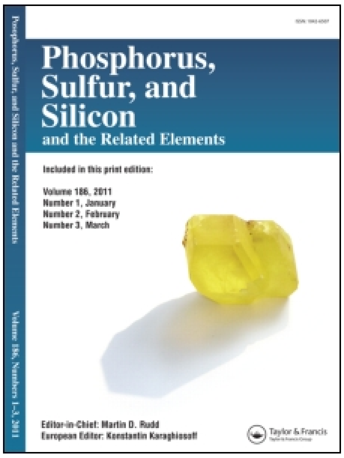

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REACTION OF α-CHLOROTOLUENE WITH ELEMENTAL SULFUR IN LIQUID AMMONIA

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α-Chlorotoluene (**1**) reacts with elemental sulfur in liquid ammonia affording dibenzyl disulfide (**2**), dibenzyl trisulfide (**3**), dibenzyl tetrasulfide (**4**), dibenzyl pentasulfide (**5**) and benzylidene benzylimide (**6**) at a low temperature such as 20°C. This reaction is presumed to be initiated by the nucleophilic attack of ammonium thioaminohydroxylate, "$H_2NS^-NH_4^+$," or dithioaminohydroxylate, "$H_2NSS^-NH_4$," formed upon treating elemental sulfur in liquid ammonia, on α-chlorotoluene (**1**). Benzylidene benzylimide (**6**) is presumed to be formed from benzylamine, which can be formed by treatment of α-chlorotoluene (**1**) with ammonia.

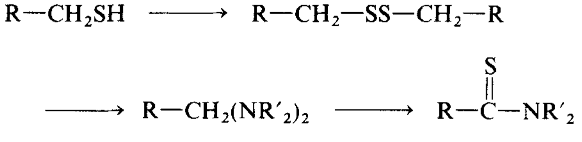
INTRODUCTION

Although there have been numerous investigations on reactions with elemental sulfur in basic media, the role and chemical behavior of both elemental sulfur and bases have not been fully understood.[2,3] One of the most interesting reactions using elemental sulfur is the Willgerodt Reaction, the mechanism of which has been investigated intensively, not only with phenacyl compounds in such amines as morpholine, but also with various unsaturated compounds in other bases.

Solutions of elemental sulfur in various amines display a rather intriguing character, some giving free radical ESR signals.[5] However there is no clear-cut understanding of the physico-chemical properties of elemental sulfur in amines, except that the system is an excellent electron donor which can supply electrons and in turn become a free radical.

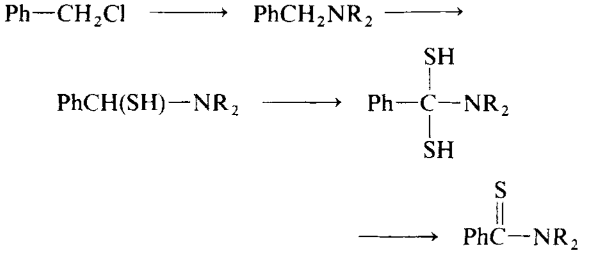
Recently we have shown that elemental sulfur dissociates in liquid ammonia giving ammonium thioaminohydroxylate, $H_2NS^-NH_4^+$, or dithioaminohydroxylate, $H_2NSS^-NH_4^+$, which can react with 4-chloronitrobenzene affording 4-nitrobenzenethiosulfenamide.[7] This means that aminothiohydroxylate or aminodithiohydroxylate, formed by dissolving elemental sulfur in liquid ammonia, should be a powerful nucleophile.

Milligan *et al.* reported that thiobenzmorpholide was obtained in the reaction of α-chlorotoluene with elemental sulfur in morpholine with no explanation of the mechanism.[8] The formation of thiobenzamide from such an α-substituted toluene derivative as α-toluenethiol was also discussed by F. H. McMillan *et al.*[9]



$$R\text{—}CH_2SH \longrightarrow R\text{—}CH_2\text{—}SS\text{—}CH_2\text{—}R \longrightarrow R\text{—}CH_2(NR'_2)_2 \longrightarrow R\text{—}\overset{\overset{\displaystyle S}{\|}}{C}\text{—}NR'_2$$

They proposed the alkylidene diamine as the intermediate in the Willgerodt–Kindler reaction. Others suggested, however, that the formation of thiobenzmorpholide takes place via the initial formation of a C—N bond, followed by thiolation and stabilization.[2] All these reactions can proceed only when the reaction mixture is heated above 100°C.



α-Chlorotoluene (**1**) reacts with elemental sulfur in liquid ammonia at a high temperature such as 125°C yielding thiobenzamide; however, some reactions can take place in this system even at room temperature. Hence, it is conceivable that the intervening intermediates of the initial stage of the Willgerodt reaction might be observable when the reaction is carried out at a relatively low temperature. Indeed, we found dibenzyl disulfide (**2**), dibenzyltrisulfide (**3**), dibenzyl tetrasulfide (**4**), dibenzyl pentasulfide (**5**) and benzylidene benzylimide (**6**) (Schiff Base) when the reaction was performed at a low temperature such as 20°C.

This paper describes details of this reaction.

EXPERIMENTAL

Materials

α-Chlorotoluene (**1**): A commercially available product (Kanto Chemical Co., Tokyo, Japan) was distilled just before use.

Elemental sulfur: A commercially available powdered elemental sulfur (Kanto Chemical Co., Tokyo, Japan) was recrystallized from carbon disulfide and then washed with ethanol just before use.

Liquid ammonia: A commercially available liquid ammonia (Nippon Kasei Co. Fukushima, Japan) was distilled just before use.

Reaction Vessel

All reactions were carried out in an all-titanium autoclave (50 ml capacity) but the solution of elemental sulfur in liquid ammonia was prepared in a transparent quartz tube.

Reaction of α-Chlorotoluene (1) with Elemental Sulfur in Liquid Ammonia.

A typical run was carried out as follows. α-Chlorotoluene (**1**), 1.27g (10 mmol), was placed in an all-titanium autoclave. The solution of elemental sulfur, 7.5 mg-atom, in 20 ml liquid ammonia prepared in a transparent quartz tube for 1h with stirring at 20°C, was charged into the evacuated autoclave. This mixture was allowed to react under various conditions (see Tables I–III). At the end of the reaction ammonia was sprayed at once together with the reaction mixture through the needle valve of the titanium autoclave into a conical flask containing 10 ml of carbon tetrachloride. After evaporation of ammonia, ammonium chloride and unreacted elemental sulfur were removed by filtration. The solution of carbon tetrachloride containing the products was used for nmr measurement after addition of 4-nitrotoluene (200 mg) as the internal standard to determine the yields of products. In this reaction the products obtained were dibenzyl disulfide (**2**), dibenzyl trisulfide (**3**), dibenzyl tetrasulfide (**4**), dibenzyl pentasulfide (**5**), benzylidene benzylimide (**6**), benzylamine (**7**) and dibenzylamine (**8**) which were identified by comparison with authentic samples.

Reaction of α-Chlorotoluene (1), α-Toluenethiol (11) and Disulfide (2) with Elemental Sulfur in Liquid Ammonia at 125°C.

The substrate (10 mmol) (5 mmol in the case of disulfide) and 20 mg-atom of elemental sulfur were placed in an all-titanium autoclave. After the autoclave was evacuated, 10 ml of liquid ammonia was charged and then the mixture was allowed to react at 125°C. At the end of the reaction, ammonia was removed by evaporation and the mixture was extracted with 20 ml of ether. The ether was removed under reduced pressure. The mixture of products was separated by column chromatography on alumina (Merck neutral) using chloroform as eluent. A yellow crystalline solid, thiobenzamide, was obtained and recrystallized from chloroform. mp 116°C, IR(KBr), 3350, 3270 and 3150 cm^{-1}(NH_2), NMR ($CDCl_3$) $\delta = 7.28$–7.92 (7H, m, NH_2 and aromatic), Found, S%, 23.1, Calcd. for C_7H_7NS, S%, 23.4%.

Reaction of Dibenzyl disulfide (2) with Liquid Ammonia at 125°C. The disulfide (**2**) (5 mmol) was placed in an all-titanium autoclave and the reaction was carried out as in the case of α-toluenethiol and elemental sulfur in liquid ammonia.

Other Reactions in Liquid Ammonia.

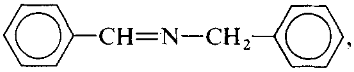
Other reactions were carried out as the reaction of α-chlorotoluene (**1**) with elemental sulfur in liquid ammonia. These reaction conditions are shown in the Table III.

Data of NMR Chemical Shift of Products and Related Compounds

Dibenzyl Disulfide (**2**) ($CDCl_3$): $\delta = 3.47$ (4H, s, $-CH_2-$)
Dibenzyl trisulfide (**3**) ($CDCl_3$): $\delta = 3.97$ (4H, s, $-CH_2-$)
Dibenzyl tetrasulfide (**4**) ($CDCl_3$): $\delta = 4.08$ (4H, s, $-CH_2-$)
Dibenzyl pentasulfide (**5**) ($CDCl_3$): $\delta = 4.16$ (4H, s, $-CH_2-$)
Benzylidene benzylimide (**6**) ($CDCl_3$): $\delta = 4.73$ (2H, s, $-CH_2-$) and 8.43 (1H, s, $-CH=$)
Benzylamine (**7**) ($CDCl_3$): $\delta = 1.17$ (2H, s, $-NH_2$) and 3.68 (2H, s, $-CH_2-$)
Dibenzylamine (**8**) ($CDCl_3$): $\delta = 1.18$ (1H, s, $=NH$) and 3.64 (4H, s, $-CH_2-$).

RESULTS AND DISCUSSION

α-Chlorotoluene (**1**) reacts with elemental sulfur in liquid ammonia affording dibenzyl disulfide (**2**), trisulfide (**3**), tetrasulfide (**4**), pentasulfide (**5**) and benzylidene benzylimide (**6**),



, under mild con-

TABLE I

Effect of amounts of elemental sulfur on reaction of α-chlorotoluene (**1**)[a] with elemental sulfur in liquid ammonia

Run	S_8 (mg atom)	Yield of product (%)[b]						
		RNH_2	R_2NH	RSSR	RSSSR	RSSSSR	RSSSSSR	$PhCH{=}N—CH_2Ph$
1	2.5	49	14	16	trace	trace	trace	13
2	5.0	28	5	23	3	3	3	29
3	7.0	11	3	28	5	4	3	41
4	10.0	0	2	27	10	4	2	50

[a] α-Chlorotoluene (**1**): 10 mmol, React. Temp.: 20°C, React Time: 4h. Liquid ammonia: 20 ml.
[b] $R{=}Ph—CH_2—$

TABLE II

Effect of reaction time on reaction[a]

Run	React. Time (h)	Yield of product (%)[b]						
		RNH_2	R_2NH	RSSR	RSSSR	RSSSSR	RSSSSSR	$Ph—CH{=}N—CH_2Ph$
1	1	23	3	40	trace	trace	trace	23
2	2	18	4	31	5	5	3	29
3	4	11	3	28	5	4	3	41

[a] α-Chlorotoluene (**1**): 10 mmol., Elemental sulfur: 7.5 mg atom, Liquid ammonia: 20 ml., React. temp.: 20°C.
[b] $R{=}Ph—CH_2—$.

dition such as 20°C for 4 hr. The amounts of the products changed with time and the amount of elemental sulfur used for the reaction. The results are summarized in Tables I and II.

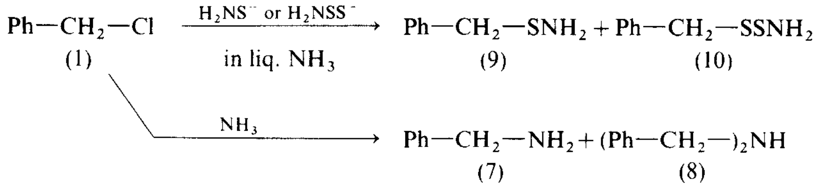
Apparently benzylamine (**7**) is formed by the reaction of α-chlorotoluene (**1**) with liquid ammonia, along with other polysulfides, which are presumed to be formed along with thioaminohydroxylate and dithioaminohydroxylate, since the nucleophiles available in this system are ammonia, thiohydroxylate and dithiohydroxylate.[6] All of the latter undergo nucleophilic substitution on a benzylic carbon atom. (Scheme I).

Although 4-nitrobenzene thiosulfenamide was obtained in the reaction of 4-chloronitrobenzene with elemental sulfur in liquid ammonia,[7] benzylsulfenamide or thiosulfenamide, (**9**) or (**10**), was not obtained in this reaction. Probably benzylsulfenamide (**9**) or thiosulfenamide (**10**), once formed in the initial stage, is attacked by thioaminohydroxylate, dithioaminohydroxylate or ammonia affording α-toluenethiolate (**11**) as shown in Scheme II.

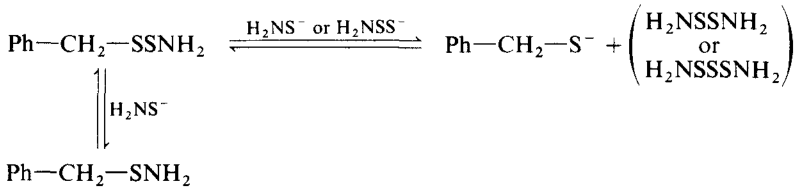
The α-toluenethiolate (**11**) thus formed would react immediately with sulfenamide or thiosulfenamide such as (**9**) or (**10**) giving dibenzyl disulfide (**2**) as in the following equation.

$$\begin{pmatrix} Ph—CH_2—SNH_2 \\ \text{or} \\ Ph—CH_2—SSNH_2 \end{pmatrix} + Ph—S^- \rightleftharpoons Ph—CH_2—SS—CH_2—Ph + \begin{pmatrix} H_2NS^- \\ \text{or} \\ H_2N^- \end{pmatrix} \qquad (1)$$

Disulfides are known to react with nucleophiles[2] such as cyanide,[10] phosphines,[11] thiols,[12] amines[13] and hydroxide,[14] but all these are reversible



SCHEME I



$$\mathrm{Ph{-}CH_2{-}SSNH_2} \overset{H_2NS^- \text{ or } H_2NSS^-}{\rightleftharpoons} \mathrm{Ph{-}CH_2{-}S^-} + \begin{pmatrix} \mathrm{H_2NSSNH_2} \\ \text{or} \\ \mathrm{H_2NSSSNH_2} \end{pmatrix}$$

$$\mathrm{Ph{-}CH_2{-}SSNH_2} \overset{H_2NS^-}{\rightleftharpoons} \mathrm{Ph{-}CH_2{-}SNH_2}$$

SCHEME II

reactions. At the initial stage of the reaction, disulfide (**2**) is considered to be formed preferentially, since the equilibrium is shifted to the right in the reaction, i.e. Eq. (1). One finds in Table I that the yield of disulfide (**2**) remained nearly constant, whereas trisulfide (**3**) increased as the amount of elemental sulfur increased (see runs 1–4 in the Table I). Formation of trisulfide (**3**), tetrasulfide (**4**) and pentasulfide (**5**) were observed. These polysulfide are presumed to be formed by the nucleophilic attack of aminothiohydroxylate or aminodithiohydroxylate on the sulfenyl sulfur atom of disulfide (**2**) and polysulfides according to Scheme III, since such a thiolate anion as aminothiohydroxylate "H_2NS^-" or aminodithiohydroxylate "H_2NSS^-" should be a good "thiophilic reagent".

The amounts of the polysulfides increased at the expense of the disulfide as the reaction proceeded as shown in the Table II (runs 1–3). This was confirmed further by the reaction of disulfide (**2**) with elemental sulfur in liquid ammonia to yield trisulfide (**3**), 24%, tetrasulfide (**4**), 7%, and pentasulfide (**5**), 6%, as shown in run 4 in Table III. Moreover, the equilibrium shown in Scheme III was clearly observed in the reaction of trisulfide (**3**) with ammonia and amine to afford disulfide (**2**), 50%, tetrasulfide (**4**), 10%, and pentasulfide (**5**), 11%, as shown in run 5 in Table III. The result obtained in run 6 in Table III is in keeping with the result in run 5.

Formation of benzylidene benzylimide (**6**) in the reaction of benzylamine with elemental sulfur was found by Sasaki *et al.* in 1971.[15] The Schiff

$$\mathrm{PhCH_2SSCH_2Ph} \overset{NH_3}{\rightleftharpoons} \mathrm{PhCH_2SNH_2 + PhCH_2SH}$$

$$\mathrm{PhCH_2SSCH_2Ph} \overset{H_2NS^-}{\rightleftharpoons} \mathrm{PhCH_2SSNH_2 + PhCH_2S^-} \rightleftharpoons \mathrm{PhCH_2SSSCH_2Ph}$$

$$\mathrm{PhCH_2SSSCH_2Ph} \overset{H_2NS^-}{\rightleftharpoons} \mathrm{PhCH_2SSSNH_2 + PhCH_2S^-} \rightleftharpoons \mathrm{PhCH_2SSSSCH_2Ph}$$

$$\mathrm{PhCH_2SSSSCH_2Ph} \overset{H_2NS^-}{\rightleftharpoons} \mathrm{PhCH_2SSSSNH_2 + PhCH_2S^-} \rightleftharpoons \mathrm{PhCH_2SSSSSCH_2Ph}$$

SCHEME III

TABLE III

Some reaction in liquid ammonia[a]

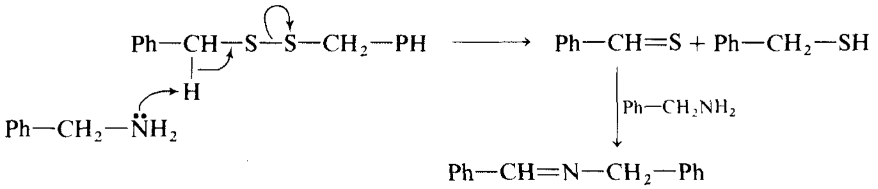
	Reactant[bc] (mmol)				Yield of product (%)[bd]				
Run	S_8	RSSR	RSSSR	RNH_2	RSSR	RSSSR	RSSSSR	RSSSSSR	Ph—CH=N—CH_2Ph
1		2.5		5.0	96				trace
2		2.5		20	92				8
3	5.0			5.0					14
4	5.0	2.5			39	24	7	6	
5			2.5	5.0	50	16	10	11	22
6	5.0		2.5		31	28	6	7	0

[a] React. Temp.: 20°C, React. Time: 4h, Liquid ammonia: 20 ml.

[b] R=Ph—CH_2—.

[c] mg-atom in the case of elemental sulfur.

[d] The yields were estimated by assuming that Schiff base, benzylidene benzylimide, was formed only from benzylamine, and polysulfides only from disulfide and trisulfide.



SCHEME IV

bases were shown by Ohno *et al.*[16] to react with elemental sulfur at room temperature yielding thiobenzamide. Formation of the Schiff base (**6**) in relatively high yields (see Tables I–III) may form according to the mechanistic scheme proposed by Sasaki *et al.*[15]

The results in runs 1 and 2 in Table III suggest that even the disulfide (**2**) is able to react with benzylamine yielding benzylidene benzylimide (**6**). The formation of benzylidene benzylimide (**6**) from disulfide (**2**) with benzylamine in liquid ammonia may be interpreted according to Scheme IV.

In this scheme proton removal from the methylene group of disulfide (**2**) with such a base as benzylamine is quite reasonable since the methylene proton adjacent to a disulfide linkage is known to be somewhat acidic[3] and α-toluenethiolate is a good leaving group.

The α-toluenethiol (**11**) thus formed would react with elemental sulfur in liquid ammonia yielding polysulfide as shown in the following equation.[17]

$$\mathrm{Ph{-}CH_2{-}SH} + \left(\begin{matrix}\mathrm{H_2NSS_xS^-} \\ \mathrm{H_2NSS_xSNH_2}\end{matrix}\right) \rightleftharpoons \mathrm{Ph{-}CH_2{-}SS_xS{-}CH_2{-}Ph}\quad (2)$$

The relatively high yield of benzylidene benzylimide (**6**), observed in the reaction of trisulfide (**3**) with benzylamine (see run 5 in Table III), is rather interesting since it implies the generation of ammonium thioaminohydroxylate, $H_2NS^-NH_4^+$, as shown below.

$$\mathrm{Ph{-}CH_2{-}SSS{-}CH_2{-}Ph} \xrightleftharpoons{NH_3} \mathrm{Ph{-}CH_2{-}SSNH_2 + Ph{-}CH_2SH}$$

$$\mathrm{Ph{-}CH_2{-}SSNH_2} \xrightleftharpoons{NH_3} \mathrm{Ph{-}CH_2{-}SNH_2 + H_2NS^-NH_4^+}$$

$$\mathrm{H_2NS^-NH_4^+} \xrightleftharpoons{NH_3} \mathrm{H_2NSS_xS^-NH_4^+} \xrightleftharpoons{NH_3} \mathrm{H_2NSS_6S^-NH_4^+} \xrightleftharpoons{NH_3} \mathrm{S_8}$$

Thus the formation of various sulfides such as disulfide (**2**), trisulfide (**3**), tetrasulfide (**4**) and pentasulfide (**5**) and that of benzylidene benzylimide (**6**) in the reaction of elemental sulfur in liquid ammonia can now be correlated.

Although thiobenzamide was not observed in this reaction at 20°C, thiobenzamide was obtained in a yield of 68 % when the reaction was carried out at 125°C for 1 hr. Similarly α-toleunethiol (**11**) was also found to react with elemental sulfur in liquid ammonia at 125°C for 6 hr. affording the thiobenzamide, 69 %, whereas disulfide (**2**) yielded thiobenzamide and α-toluenethiol (**11**) in yields of 42 % and 41 %, respectively, upon treatment with liquid ammonia alone at 125°C. The yield of thiobenzamide increased to 90 % when disulfide (**2**) was treated with elemental sulfur in liquid ammonia at 125°C for 6 hr.

All these observations seem to indicate that the reaction of α-chlorotoluene (**1**) with elemental sulfur in liquid ammonia gives, at low temperatures, benzylidene benzylimide (**6**),[16] disulfide (**2**) and polysulfide, all of which are legitimate intermediates, and give thiobenzamide when the reaction with elemental sulfur in liquid ammonia or amines is carried out at high temperatures.

REFERENCES AND NOTES

1. Present address; Chisso Ltd., Ichihara, Chiba 299–01, Japan.
2. S. Oae, *Organic Chemistry of Sulfur* (Plenum, New York, 1977).
3. S. Oae, *Chemistry of Organic Sulfur Compounds* (*Yuki Io Kagobutsu no Kagaku*), Kagaku–Dojin, Kyoto (1968).
4. (a) C. Willgerodt, *Ber.*, **20**, 2467 (1887). (b) C. Willgerodt, *Ber.*, **21**, 534 (1888).
5. T. H. Kim and J. F. Bunnett, *J. Am. Chem. Soc.*, **92**, 7463 (1970).
6. (a) R. Sato, K. Araya, Y. Takikawa, S. Takizawa, and S. Oae, *Phosphorus and Sulfur*, **5**, 245 (1978). (b) R. Sato, S. Takizawa, and S. Oae, *Phosphorus and Sulfur*, **7**, 229 (1979). R. Sato, K. Araya, Y. Takikawa, S. Takizawa, and S. Oae, *Phosphorus and Sulfur*, in press.
7. R. Sato, T. Sato, K. Segawa, Y. Takikawa, S. Takizawa, and S. Oae, *Phosphorus and Sulfur*, **7**, 217 (1979).

8. B. Milligan and J. M. Swan, *J. Chem. Soc.*, **1961**, 1194.
9. (a) F. H. McMillan, *J. Am. Chem. Soc.*, **70**, 808 (1948). (b) F. H. McMillan and J. A. King, *J. Am. Chem. Soc.*, **70**, 4143 (1948).
10. (a) O. Gawron, S. Mahbooh, and J. Fernando, *J. Am. Chem. Soc.*, **86**, 2283 (1964). (b) R. G. Hiskey and F. I. Carrol, *J. Am. Chem. Soc.*, **83**, 4644 (1961).
11. M. Grayson and C. E. Farley, *J. Org. Chem.*, **32**, 236 (1967).
12. G. Dolman, J. McDermed, and G. Gorin, *J. Org. Chem.*, **29**, 1480 (1964).
13. Y. Minoura, *Nippon Gomu Kyokaishi*, **24**, 263 (1951).
14. G. Papapalard, *Gazz. Chim. Ital.*, **90**, 648 (1960).
15. Y. Sasaki and F. D. Olsen, *Can. J. Chem.*, **49**, 283 (1971). Their proposed mechanism is roughly the following.

$$\mathrm{PhCH_2NH_2} \xrightleftharpoons{\mathrm{S_8}} \mathrm{PhCH_2NH{-}S_a{-}NHCH_2Ph}$$
$$\rightleftharpoons \mathrm{PhCH{=}N{-}S_b{-}N{=}CHPh} \rightleftharpoons$$
$$\mathrm{Ph{-}CH{=}NH} \xrightleftharpoons{\mathrm{PhCH_2NH_2}} \mathrm{Ph{-}CH{=}N{-}CH_2{-}Ph}$$

16. A. Ohno and N. Kito, Japan Pat. 7225144.
17. Although McMillan *et al.* proposed that α-toluenethiol can be oxidized catalytically with elemental sulfur in amines, the formation of disulfide and polysulfide should proceed via thiophilic sunstitution of such thiolate anion as thioaminohydroxylates, $\mathrm{H_2NSS_x^-}$, with α-toluenthiolas follows.

$$\mathrm{PhCH_2{-}SH} \xrightleftharpoons{\mathrm{H_2NSS_x^-}} \mathrm{PhCH_2{-}SSNH_2}$$
$$\xrightleftharpoons{\mathrm{PhCH_2SH}} \mathrm{PhCH_2SSCH_2Ph}$$