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REACTIONS OF DIAMINO DISULFIDES, DIAMINO SULFIDES, AND DIAMINO SULFOXIDES WITH p-TOLUENESULFINIC ACID

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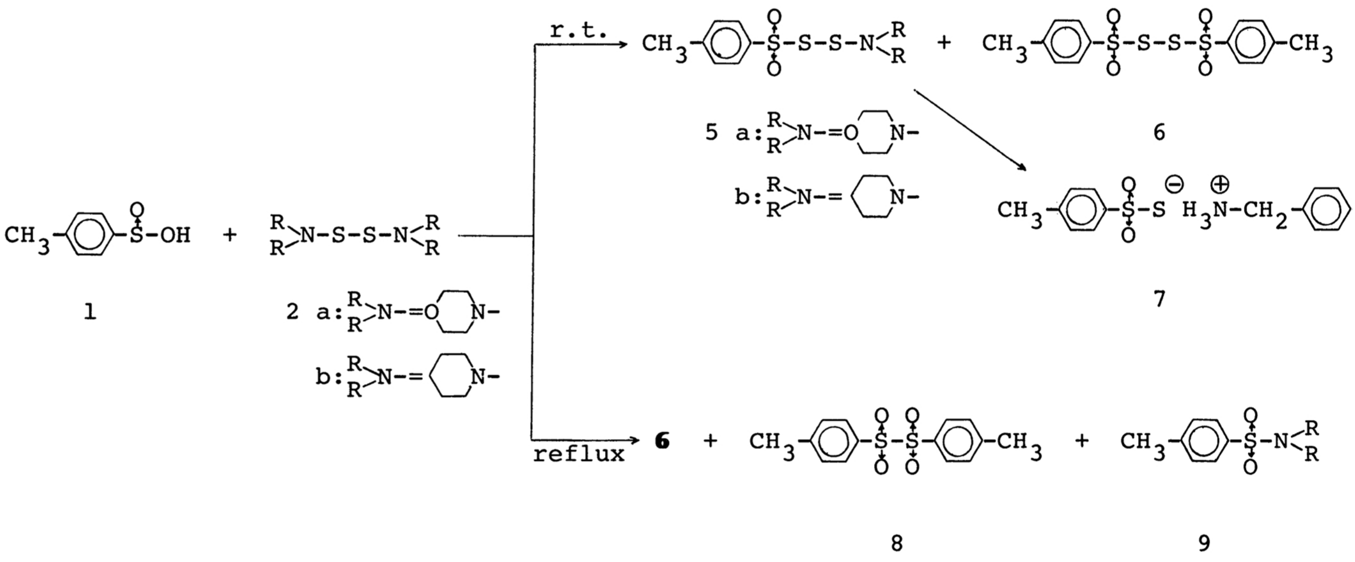
The reactions of diamino disulfides (2) and diamino sulfides (3) with p-toluenesulfinic acid (1) were found to give new types of compounds, amino p-toluenesulfonyl disulfides (5) and amino p-toluenesulfonyl sulfides (10), respectively. On the other hand, the reaction between dimorpholino sulfoxide (4) and **1** gave p-toluenesulfinylmorpholide (13).

It is well known that divalent sulfur atoms undergo both nucleophilic and electrophilic substitutions. The acid catalyzed reactions of disulfides[1,2] and sulfides[3,4] with sulfinic acids are kinetically studied in detail by Kice, and the both reactions are revealed to proceed through the electrophilic attack of cationic species, sulfinium cations, which are initially formed through protonation to sulfinic acids, on the sulfur atoms of disulfides and sulfides.

We newly examined the reactions of a few diamino disulfides (2),[5] diamino sulfides (3),[6] and dimorpholino sulfoxide (4)[7] with p-toluenesulfinic acid (1). The reaction of **1** with two equimolar amounts of dimorpholino disulfide (2a) and dipiperidino disulfide (2b) in dichloromethane proceeded smoothly at room temperature. After two hours, the mixture was washed with o.5M hydrochloric acid and then with water twice, dried over sodium sulfate, and evaporated under reduced pressure. Trituration of the residue with cold ethanol followed by recrystallization from hexane gave compounds of a new type, i.e., morpholino p-toluenesulfonyl disulfide (5a) and piperidino p-toluenesulfonyl disulfide (5b) in 62% and 32% yields, respectively. Soluble part in ethanol provided bis(p-toluenesulfonyl) disulfide (6) as the by-product in 7% and 3% yields in each case. On the other hand, when the same reactions were carried out under refluxing dichloromethane, the compound **6** was obtained in 61% and 59% yields, respectively, instead of **5**, with small amounts of di-p-tolyl disulfone (8) and p-toluenesulfonamides (9).



In the product **5**, the isomeric structure, amino p-toluenesulfinyloxy disulfide is also possible. The IR spectra of **5** exhibited absorptions assignable to the sulfonyl group near 1140 and 1330 cm^{-1}. The ^{1}H-NMR spectra showed characteristic signals due to the p-tolyl group and the morpholino or piperidino group. The mass spectra indicated the molecular ion peaks corresponding to **5**. In addition, the product **5** reacted with benzylamine in dichloromethane at room temperature to give benzylamminium p-toluenethiosulfonate (7). The structure of **7** was confirmed by identification with the IR spectrum of the authentic sample prepared from sodium p-toluenethiosulfonate and benzylamine. These results supported the assigned structure **5** rather than the isomeric structure. The spectral data of **5** are summarized in Table 1. The compounds **6**, **8**, and **9** were identified by comparison of the spectral data with those of authentic samples prepared by the alternative methods.[8,9,10]

The reactions of dimorpholino sulfide (3a) and dipiperidino sulfide (3b) with **1** were conducted under the same conditions applied for the reaction of **2** with **1**. Novel compounds, morpholino p-toluenesulfonyl sulfide (10a) and piperidino p-toluenesufonyl sulfide (10b) were isolated in 60% and 25% yields, respectively, accompanying small amounts of bis(p-toluenesulfonyl) sulfide (11) as the by-product in both cases. Analogously to the reaction of **1** with **2**, the compound **11** was obtained in 64% and 63% yields, respectively, under refluxing conditions, though any **8** and **9** could not be isolated.

The IR spectra of **10** exhibited absorptions due to the sulfonyl group near 1130 and 1300 cm^{-1}. The ^1H-NMR spectra of **10** indicated characteristic signals corresponding to p-tolyl protons and morpholino or piperidino methylene protons. These spectral patterns extremely resemble those of **5**. The mass spectra of the both **10a** and **10b** showed the respective molecular ion peaks. The elementary analyses also gave satisfactory agreement with the assigned structure **10**. The spectral data were summarized in Table 1.

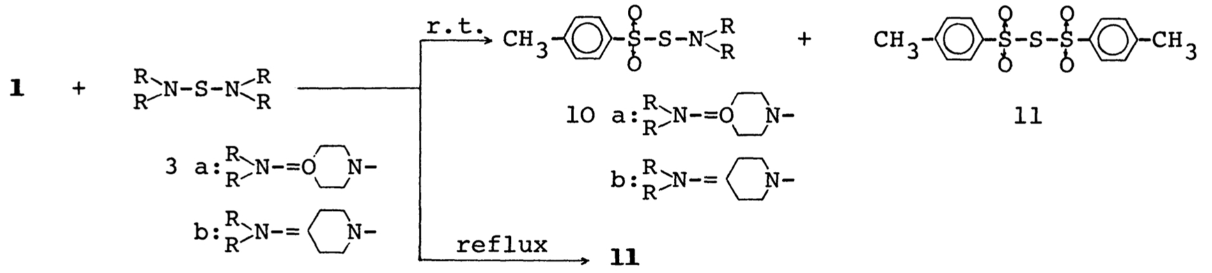
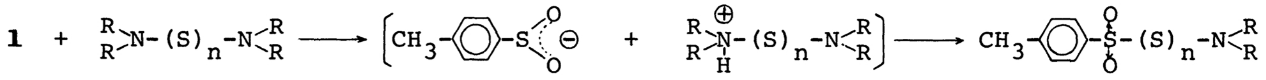


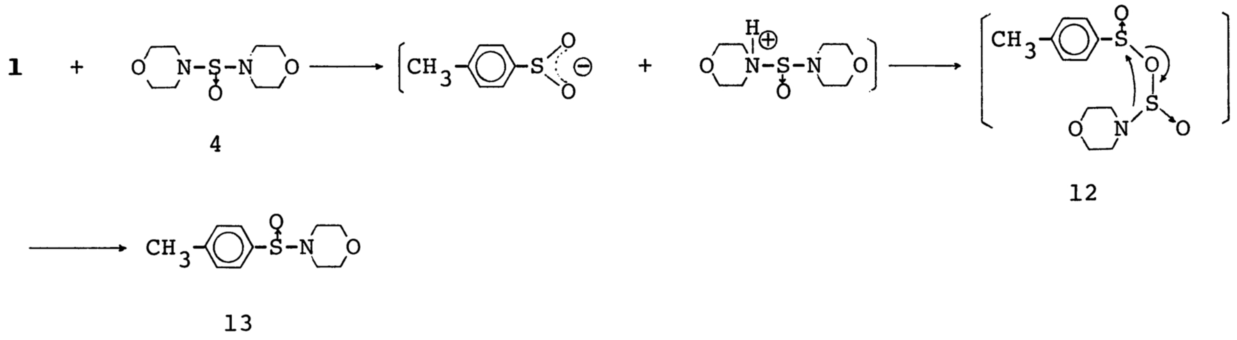
Table 1 Amino p-Toluenesulfonyl Disulfide (5) and Amino p-Toluenesulfonyl Sulfide (10)

Compd.	Mp (°C)	IR ν cm^{-1} SO_2	^1H-NMR (δ) CH_3(s)	arom.(d)	$N-CH_2$(m)	OCH_2 or CH_2-CH_2(m)	Mass (M^+)
5a	78-79	1140, 1330	2.40	7.33, 7.83	2.85-3.20	3.40-3.97	305
5b	77-78	1145, 1330	2.45	7.32, 7.82	2.85-3.20	1.15-1.95	303
10a	104-105	1135, 1300	2.46	7.31, 7.81	3.15-3.50	3.50-3.85	273
10b	65-67	1130, 1300	2.45	7.30, 7.80	3.10-3.60	1.15-1.85	271

It is known that the sulfinate anions generally behave as ambident S- and O-nucleophiles.[11)] The reactions of **2** and **3** with **1** are presumed to be initiated by nucleophilic attacks of the sulfinate S-nucleophile on the sulfur atoms of protonated **2** and **3**, resulting in heterolytic cleavage of the S-N bonds.



Contrary to the above results, the reaction of dimorpholino sulfoxide (4) with **1** gave 49% of p-toluenesulfinylmorpholide (13) in comparatively pure form, with the evolution of sulfur dioxide. In the reaction with **4**, if the sulfinate anion reacts as S-nucleophile, the corresponding sulfonamide would be formed. This is not the case, however. When the same reaction was carried out in the presence of diethylamine, **13** was isolated as the sole product without any detectable formation of cross reaction product. These facts suggest that the sulfinate anion behaves as an O-nucleophile to give primarily **12** which affords eventually **13** through the following intramolecular degradation.



Such a difference in the chemical behavior of **4** from **2** and **3** toward **1** would be explained in terms of the HSAB principle. Namely, the soft sulfenyl sulfur atoms of **2** and **3** may easily react with the soft sulfinate S-nucleophile rather than the hard sulfinate O-anion, whereas the hard sulfinyl sulfur of **4** would prefer to react with the latter hard nucleophilic site of ambident sulfinate.

Further detailed studies are currently in progress.

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