CHEMISTRY LETTERS, pp. 1603-1606, 1983.

FACILE DEIMINATION OF SULFIMIDES AND SULFODIIMIDES WITH ELEMENTAL SULFUR CATALYZED OR UNCATALYZED BY AMINES

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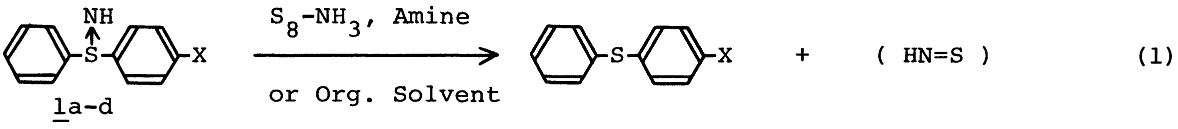
Sulfimides and sulfodiimides were readily deiminated with elemental sulfur catalyzed or uncatalyzed by amines affording corresponding sulfides and its derivatives under mild conditions in excellent yields.

The chemistry of sulfimides and its derivatives is a subject of current interest in the preparation and characterization.1) Less attention has been, however, paid to the reduction of sulfimides and sulfodiimides to sulfides, although few reagents have been used to achieve the reduction satisfactorily. The studies on the deimination reagents have been developed by some workers, that is, p-toluenesulfonyl nitrite,2) phosphorus pentasulfide,3) diazomalonate,4) thiol/trimethyl chloride5) and trifluoroacetic anhydride/sodium iodide system or titanium chloride6) have been used as deimination reagents. Oae and co-workers have reported the deiminations of N-tosyl sulfimides and sulfoximides with molten sulfur at very high temperature such as 150-160 °C.7) Thus, these procedures were carried out under drastic conditions or the deimination reagents used were very difficult to obtain or handle. In the course of our investigations on the reactions of organosulfur compounds with elemental sulfur/liquid ammonia and amines system,8) we found a new deimination of sulfimides and related compounds.

We wish to report a facile and convenient deimination of sulfimides and related compounds with elemental sulfur catalyzed or uncatalyzed by amines under mild conditions such as 20 °C affording corresponding sulfides as shown in Eq, 1.

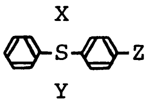
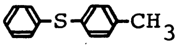
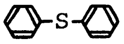
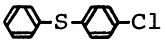
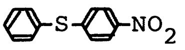
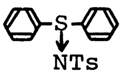
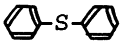
Typical procedure is as follows. Sulfimides, sulfoximides and



sulfodiimides used in the present reaction were synthesized by the known procedure in the literatures.9) Substrate(1 mmol) and elemental sulfur(1 mg atom) were taken into a flask containing amine or organic solvent(10 ml). When liquid ammonia was used, all titanium autoclave was employed for avoiding corrosion. After evacuation liquid ammonia(10 ml) was charged into the autoclave.
A reaction mixture obtained by usual work up after evaporation of ammonia, amines or organic solvent was chromatographed on silica gel(Wako gel C-300) using chloroform as eluent. Resulted products in this reaction were identified by comparing these NMR, IR and Mass spectra with those of the authentic samples. These results are summarized in Table 1.

Unsubstituted sulfimides(1a, b, c) were easily deiminated to the corresponding sulfides(2a, b, c) with elemental sulfur in liquid ammonia(runs 1, 3, 9) under mild conditions such as 20 °C in very excellent yields. The deiminations were also observed in organic solvent such as methanol(runs 2, 4, 13), chloroform(run 5), acetonitrile(run 6) and benzene(run 7) in the absence of amines, but no reaction occurred without heating. The sulfimides bearing electron-withdrawing group such as nitro group, 1d, was less reduced with elemental sulfur (run 13). These facts suggest that the deimination is catalyzed by added amines (runs 7 and 8) and depends on the basicity of imino group in sulfimides. It should be noted that sulfodiimides, 1e and 1f, were also readily deiminated with elemental sulfur in liquid ammonia to give the corresponding sulfimide, 2e, and sulfide, 2b(runs 14 and 15). Whereas, deimination of sulfoximide(1g) and N-tosylsulfimide(1h) were unsuccesful(runs 16 and 17). This is interpreted in terms of the lower basicity of sulfoximide than that of sulfimide.10) Thus a selectivity of deimination towards free imino group was observed.
Unfortunately, the expected sulfur imides, HN=S, (Eq. 1) could not be still detected cleanly at present stage. The studies on the mechanism of these reactions involving the formation of sulfur imide are now in progress.

Table 1. Deimination of Sulfimides and Sulfodiimides with Elemental Sulfur in Liquid Ammonia, Amines or Organic Solvent

Run[a]	Substrate: 				Solvent	Reaction		Product		Yield[b] /%
	X	Y	Z			Temp/°C	Time/h			
1	NH	-	CH_3	1a	NH_3	20	2		2a	100
2	NH	-	CH_3	"	CH_3OH	60	0.5	"	"	100
3	NH	-	H	1b	NH_3	40	2		2b	96
4	NH	-	H	"	CH_3OH	60	0.5	"	"	93
5	NH	-	H	"	$CHCl_3$	60	0.5	"	"	70
6	NH	-	H	"	CH_3CN	40	6	"	"	88
7	NH	-	H	"	C_6H_6	40	2	"	"	68
8[c]	NH	-	H	"	C_6H_6 + Propylamine	40	2	"	"	83
9	NH	-	Cl	1c	NH_3	40	2		2c	100
10	NH	-	Cl	"	Propylamine	20	2	"	"	95
11	NH	-	Cl	"	Diethylamine	20	2	"	"	88
12	NH	-	Cl	"	Triethylamine	20	2	"	"	82
13	NH	-	NO_2	1d	CH_3OH	60	0.5		2d	55
14	NH	NTs	H	1e	NH_3	100	2		2e	93
15	NH	NH	H	1f	NH_3	100	2		2b	89
16	NH	O	H	1g	NH_3	100	2	no reaction		
17	NTs	-	H	1h	NH_3	100	2	no reaction		

a) Substrate: 1 mmol, Elemental Sulfur: 1 mg atom,

b) Isolated Yield based on the substrate. c) Amine (3 ml) was added.

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(Received August 10, 1983)