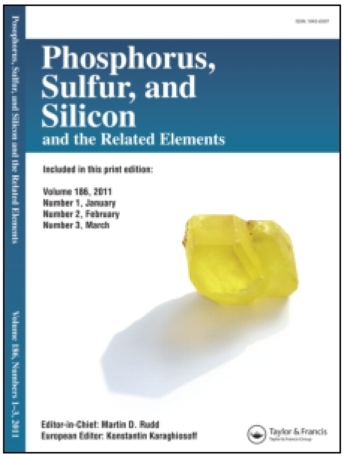

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Nozaki, Kenji , Yoshihara, Masakuni , Enomura, Kazunori , Matsubara, Yoshio and Maeshima, Toshihisa(1985) 'Reduction of Sulfoxides by Thioformamizium Salts', Phosphorus, Sulfur, and Silicon and the Related Elements, 22: 1, 131 — 133

To link to this Article: DOI: 10.1080/03086648508073362

URL: http://dx.doi.org/10.1080/03086648508073362

Phosphorus and Sulfur, 1985, Vol. 22, pp. 131–133
0308-664X/85/2201-0131/$10.00/0

SHORT COMMUNICATION
Reduction of Sulfoxides by Thioformamizium Salts

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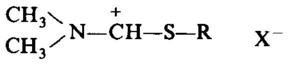
(*Received August 1, 1984; in final form September 17, 1984*)

Iminium salts are known to be useful for the preparation of carboxylic esters, carboxyamides, lactones and alkyl halides.[1,2] This paper describes the reduction of sulfoxides to corresponding sulfides by treating with thioformamizium salts Ia–c.



$$(CH_3)_2\overset{+}{N}{=}CH{-}S{-}R \quad X^-$$

(Ia) R: CH_2Ph X: Cl
(Ib) R: CH_3 X: OTs
(Ic) R: CH_2CH_3 X: OTs

N,*N*-Dimethyl-*S*-benzylthioformamizium chloride (Ia) was prepared by the reaction of *N*,*N*-dimethylthioformamide (DMTF) with an equimolar amount of benzyl chloride according to the method of Arnold.[3] Yield 70%. mp 58–60°C. *N*,*N*-Dimethyl-*S*-methylthioformamizium tosylate (Ib) and *N*,*N*-dimethyl-*S*-ethylthioformamizium tosylate (Ic) were prepared by heating DMTF with equimolar amounts of methyl and ethyl *p*-toluenesulfonates, respectively, in dry nitrogen atmosphere at 65°C for 2 hr.[4] Colorless oils. Yield: Ib 80% and Ic 82%, respectively. Spectral data of thioformamizium salts are summarized in Table I.

Typical procedure of synthesis of sulfide from sulfoxide with the use of thioformamizium chloride (Ia) was as follows. A mixture of sulfoxide (2 mmol) and an equimolar amount of Ia in dry chloroform (5 ml) was stirred in dry nitrogen atmosphere at 50°C for 4 hr. The reaction was monitored by TLC and GLC. The solvent was evaporated and the residue was subjected to column chromatography (solvent, benzene) to isolate the products. The results are given in Table II. Corresponding sulfides, dimethylformamide, and benzyl chloride were obtained in fairly good yields.

Reduction of sulfoxides to the corresponding sulfides was also found to take place upon heating with equimolar amounts of the thioformamizium tosylates (5 mmol) Ib or Ic, and tetra-*n*-butylammonium chloride (5 mmol) in chloroform (5 ml) at 50°C for 4 hr, followed by the work-up described above. It is noted that no reaction of sulfoxide took place upon heating with equimolar amounts of thioformamizium tosylates (5 mmol) alone in chloroform (5 ml) at 50°C for 12 hr.

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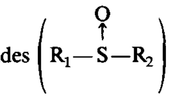
TABLE I

^{1}H-NMR and IR spectra of thioformamizium salts

Salt	^{1}H-NMR (ppm)					IR (cm^{-1})
	CH	CH_3N	CH_2	CH_3	Ph	$\nu_{C=O}$
Ia	11.55	3.31 3.73	4.90	—	7.19	1615
b	9.98	2.72 3.12	—	2.28	—	—
c	9.98	3.23 2.28	—	1.33	—	—

TABLE II



The reaction of several sulfoxides $\left(R_1-\overset{\overset{O}{\uparrow}}{S}-R_2\right)$ with the thioformamizium salts in chloroform at 50°C

Salt	Sulfoxide		Product	Yield[c] (%)
	R_1	R_2		
Ia	Me	Me	Me—S—Me	82[d]
			$PhCH_2Cl$	73
			DMF	65[d]
	$PhCH_2$	$PhCH_2$	$PhCH_2$—S—CH_2Ph	53
			$PhCH_2Cl$	46
	Ph	Ph	Ph—S—Ph	70
			$PhCH_2Cl$	68
	Ph	Me	Ph—S—Me	75
			$PhCH_2Cl$	68
Ib[b]	Me	Me	Me—S—Me	70[d]
			DMF	68[d]
	Me	$PhCH_2$	Me—S—CH_2Ph	88
			DMF	71[d]
	Et	$PhCH_2$	Et—S—CH_2Ph	88
			DMF	60[d]
Ic[b]	Me	$PhCH_2$	Me—S—CH_2Ph	79
			DMF	60[d]
	$PhCH_2$	$PhCH_2$	$PhCH_2$—S—CH_2Ph	61
			DMF	53[d]

[a] Sulfoxide, 5 mmol; Thioformamizium salt, 5 mmol; Chloroform, 5 mmol; Reaction time, 4 hr.

[b] An equimolar amount of tetra-*n*-butylammonium chloride was added.

[c] Isolated yield.

[d] Determined by Gas-Chromatography.

It is also noted that *N*,*N*-dimethylaniline *N*-oxide (5 mmol) was converted to *N*,*N*-dimethylaniline (88%), along with the formation of DMF (63%), dibenzyl disulfide (45%), benzyl chloride (28%), upon treating with Ia (5 mmol) in dry chloroform (5 ml) at room temperature for 6 hr. No reduction of pyridine *N*-oxide (5 mmol) took place upon heating with an equimolar amount of Ia in dry chloroform (5 ml) at 65°C for 12 hr.

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