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SHORT COMMUNICATION

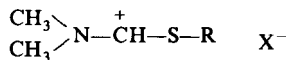
Reduction of Sulfoxides by Thioformamizium Salts

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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.



(Ia) R: CH₂Ph X: Cl

(Ib) R: CH₃ X: OTs

(Ic) R: CH₂CH₃ 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
¹H-NMR and IR spectra of thioformamizium salts

Salt	¹ H-NMR (ppm)					IR (cm ⁻¹) ν _{C=O}
	CH	CH ₃ N	CH ₂	CH ₃	Ph	
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 $\left(\begin{array}{c} \text{O} \\ \uparrow \\ \text{R}_1-\text{S}-\text{R}_2 \end{array} \right)$ 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 ₂ Cl	73
			DMF	65 ^d
	PhCH ₂	PhCH ₂	PhCH ₂ —S—CH ₂ Ph	53
	Ph	Ph	PhCH ₂ Cl	46
			Ph—S—Ph	70
			PhCH ₂ Cl	68
	Ph	Me	Ph—S—Me	75
Ib ^b	Me	Me	PhCH ₂ Cl	68
			Me—S—Me	70 ^d
			DMF	68 ^d
	Me	PhCH ₂	Me—S—CH ₂ Ph	88
	Et	PhCH ₂	DMF	71 ^d
			Et—S—CH ₂ Ph	88
Ic ^b	Me	PhCH ₂	DMF	60 ^d
			Me—S—CH ₂ Ph	79
			PhCH ₂ —S—CH ₂ Ph	61
	PhCH ₂	PhCH ₂	DMF	53 ^d

^aSulfoxide, 5 mmol; Thioformamizium salt, 5 mmol; Chloroform, 5 mmol; Reaction time, 4 hr.

^bAn equimolar amount of tetra-*n*-butylammonium chloride was added.

^cIsolated yield.

^dDetermined 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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