

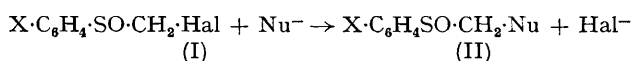
## Kinetics of Nucleophilic Substitution of $\alpha$ -Halogeno-sulphoxides

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**Summary**  $\alpha$ -Halogenomethyl sulphoxides react with  $\text{Pr}^n\text{O}^-$  and  $\text{EtS}^-$  in  $\text{Pr}^n\text{OH}$  via  $S_N2$  substitution;  $\alpha$ -halogeno-ethyl and isopropyl derivatives react more slowly:  $S_N2$  reactions are greatly retarded by steric effects and  $S_N1$  reactions by the effect of the SO group.

ALTHOUGH syntheses of  $\alpha$ -halogeno-sulphoxides have been reported,<sup>1</sup> the behaviour of this class of compound is largely unknown. The Finkelstein reaction of chloro-sulphoxides has been investigated,<sup>2,3</sup> and a study<sup>4</sup> of nucleophilic substitution has appeared, but no kinetic data were reported in the latter case. The reactivity of  $\alpha$ -halogeno-sulphoxides towards nucleophilic substitution was thought to be low.<sup>3,5</sup> This is in contrast<sup>2</sup> with the well known reactivity of phenacyl halides. We now report on the kinetics of the nucleophilic substitution of  $\alpha$ -chloro- and  $\alpha$ -bromo-methyl aryl sulphoxides by  $\text{NaOPr}^n$  and  $\text{EtSNa}$  in  $\text{Pr}^n\text{OH}$ .



- |                              |                              |
|------------------------------|------------------------------|
| (Ia) X= <i>p</i> -Me, Hal=Cl | (Id) X= <i>p</i> -Me, Hal=Br |
| (Ib) X= <i>p</i> -Cl, Hal=Cl | (Ie) X= <i>p</i> -Cl, Hal=Br |
| (Ic) X= <i>m</i> -Cl, Hal=Cl |                              |

In the reaction with  $\text{EtS}^-$ , the corresponding  $\alpha$ -ethylthio-methyl aryl sulphoxides (II) were obtained in  $\geq 90\%$  yield. In the reaction with  $\text{Pr}^n\text{O}^-$ , together with  $\alpha$ -propoxymethyl aryl sulphoxides (II), the corresponding thiosulphinates (III) were obtained, *i.e.*, the products of thermal rearrangements of ethers (II). T.l.c. analysis showed that only for conversion  $\geq 60\%$  were noticeable quantities of thiosulphinate formed, the amount increasing with time.

Ethers (II) are converted into thiosulphinates (III) under the conditions of the reaction in the absence of nucleophiles. A similar transformation has been observed in the case of  $\alpha$ -methoxymethyl aryl sulphoxides.<sup>6</sup>

Reaction of (I) with  $\text{EtS}^-$  and  $\text{Pr}^n\text{O}^-$  follows second-order kinetics up to at least 80% conversion. Rate constants and activation parameters are given in the Table.

The ratios  $k(\text{Br})/k(\text{Cl})$ , *ca.* 12 and 33 for  $\text{Pr}^n\text{O}^-$  and  $\text{EtS}^-$ , respectively, the ratios  $k(\text{EtS}^-)/k(\text{Pr}^n\text{O}^-)$ , *ca.*  $8 \times 10^2$  and  $3 \times 10^3$  in the case of  $\alpha$ -chloro- and  $\alpha$ -bromo-sulphoxides, respectively, and the activation parameters (see Table) all support an  $S_N2$  mechanism.<sup>7</sup> The reaction is favoured by electron-withdrawing groups, as in the Finkelstein reactions of  $\alpha$ -halogenosulphones.<sup>2</sup>

The reactivity of (I) is comparable with that of 1-bromo-3-phenylpropane (see Table),<sup>†</sup> probably resulting from a

<sup>†</sup> A direct comparison with the reactivity of the corresponding  $\alpha$ -halogenomethyl sulphones was not possible since under the conditions of the reaction reduction to methyl sulphones occurs instead of nucleophilic substitution.<sup>8</sup>

Rate constants for the reaction of (I) with Pr<sup>n</sup>O<sup>-</sup> and EtS<sup>-</sup> in Pr<sup>n</sup>OH

Substrate	Nucleophile	Temp./°C	10 <sup>3</sup> k/1 mol <sup>-1</sup> s <sup>-1</sup>	E <sub>a</sub> /kcal mol <sup>-1</sup>	ΔS <sup>*</sup> /e.u.
(Ia)	Pr <sup>n</sup> O <sup>-</sup>	80	0.23		
(Ib)	"	80	0.70		
(Ic)	"	80	0.79		
(Id)	"	80	2.75	20.3 <sup>a</sup>	-15 <sup>b</sup>
(Ie)	"	80	7.61		
PhCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br	"	80	3.3		
(Ia)	EtS <sup>-</sup>	50	21.8	16.1 <sup>a</sup>	--18.7 <sup>b</sup>
(Ib)	"	50	54.6		
(Ic)	"	50	61.4		
(Id)	"	40	346	15.1 <sup>c</sup>	--14.8 <sup>b</sup>
(Ie)	"	40	864		
(Id)	"	30	148		
PhCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br	"	30	49		

<sup>a</sup> From measurements at 80°, 70°, and 60°. <sup>b</sup> At 60°. <sup>c</sup> From measurements at 60°, 50°, 40°, 30°.

balance between the electron-withdrawing effect of the SO group, which should promote nucleophilic attack,<sup>2</sup> and a field and steric effect which should retard S<sub>N</sub>2 displacement, as found in α-halogenosulphones.<sup>2</sup> α-Halogenoethyl and α-halogenoisopropyl sulphoxides react with alkoxides and thiols only after longer reaction times to give the products

of β-substitution, *via* elimination-addition.<sup>6,9</sup> This illustrates the important role played by steric effects in S<sub>N</sub>2 displacements. In contrast, the formation of carbocations is likely to be greatly hindered by the presence of the SO group.

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<sup>9</sup> Unpublished results.