Nucleophilic Substitution in α-Halogeno-sulphoxides. Part II.[1] Dependence of the Reaction Mechanism on Structural Factors and on the Nature of Nucleophile

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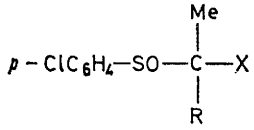
Nucleophilic substitutions on α-halogeno-sulphoxides proceed through two competitive mechanisms, a direct S_N2 substitution and an elimination–addition process. The prevalence of either of the paths depends on the structure of the substrate and on the nature of the nucleophile. S_N2 Displacement occurs in the reaction of α-halogenoethyl sulphoxides with EtS^-, while elimination–addition takes place in the reaction of these substrates with Pr^nO^- and in the reaction of 1-halogeno-1-methylethyl derivatives with both nucleophiles.

ALTHOUGH nucleophilic substitutions in α-halogeno-sulphides and -sulphones have been widely investigated,[2-6] little work [1,7,8] has been carried out on the corresponding reaction of α-halogeno-sulphoxides. It has been shown [1] that α-halogenomethyl sulphoxides react with Pr^nO^- and EtS^- in Pr^nOH *via* S_N2 substitution, their reactivity being comparable with that of primary alkyl halides and much lower than that of phenacyl halides.[9] We wished to find out if the mechanism of the reaction depends on branching of the alkyl chain and the nature of the nucleophile and therefore examined the behaviour of 1-halogeno-ethyl and -1-methylethyl sulphoxides (I)—(IV) in reaction with Pr^nO^- and EtS^-. *p*-Chlorophenyl derivatives were chosen in order to increase the rate of nucleophilic substitution since it had been previously shown that the reactions are favoured by electron-withdrawing groups.[1]

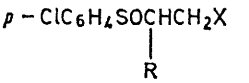
Compounds (I)—(IV) were prepared by α-halogenation of the corresponding sulphoxides or sulphides with (dichloroiodo)benzene or bromine and silver nitrate in the presence of pyridine.[10] As previously found for similar substrates,[10] when the α-carbon atom is prochiral, as in the case of ethyl derivatives, only one of the two possible diastereoisomers, (Ia) and (IIa), respectively, was obtained. Compound (Ib) was obtained from the epimer (Ia) *via* the alkoxysulphonium salt, followed by hydrolysis which proceeds with inversion at the sulphur atom.[11]

Reactions with Nucleophiles.—Reaction of compounds (I)—(IV) with Pr^nO^- were carried out in Pr^nOH at 80° in the presence of a small excess of nucleophile (1.2—1.5 mol per mol of substrate). Starting from the chloroethyl and bromoethyl sulphoxides (Ia) and (IIa) the corresponding 2-(*p*-chlorophenylsulphinyl)ethyl propyl ether (V) was obtained in 80% yield after 31 and 17 h, respectively. Under the same conditions the isopropyl derivatives (III) and (IV) gave after 40 and 18 h, respectively, the product of elimination–addition, 2-(*p*-chlorophenylsulphinyl)propyl propyl ether (VI), as a mixture of the two possible diastereoisomers, in *ca.* 75% yield.

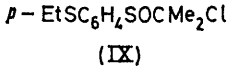
α-Chloroethyl (Ia) and α-bromoethyl sulphoxide (IIa) reacted with EtS^- in Pr^nOH at 60° to give 1-(*p*-chlorophenylsulphinyl)ethyl ethyl sulphide (VII) in 81 and 92% yield, respectively, after 40 and 20 h, respectively.



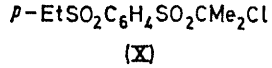
(Ia,b) R = H X = Cl
(IIa,b) R = H X = Br
(III) R = Me X = Cl
(IV) R = Me X = Br
(VIIa,b) R = H X = SEt



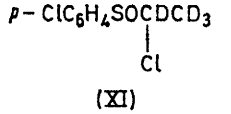
(V) R = H X = OPr^n
(VIa,b) R = Me X = OPr^n
(VIIIa,b) R = Me X = SEt



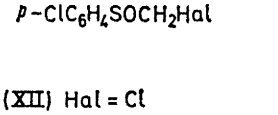
(IX)



(X)



(XI)



(XII) Hal = Cl
(XIII) Hal = Br

The reaction is not stereospecific, contrary to all expectations for a direct S_N2 nucleophilic substitution. Sulphoxide (VII) was a mixture of the two possible diastereoisomers (VIIa and b) in a *ca.* 1 : 1 ratio, as indicated by ^1H n.m.r. spectroscopy and by chemical evidence (see Experimental section). Furthermore the same mixture of compounds (VIIa and b) was obtained when the reaction was performed either with α-chloroethyl sulphoxide (Ia or b). Indeed we have shown that

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[7] T. Numata and S. Oae, *Bull. Chem. Soc. Japan*, 1972, **45**, 2794.
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[11] C. R. Johnson and D. McCants, *J. Amer. Chem. Soc.*, 1965, **87**, 5404.

α-halogenoethyl sulphoxides (I) and (II) as well as the corresponding sulphides (VIIa and b) are easily epimerized under the reaction conditions.

Reaction of 1-bromo-1-methylethyl *p*-chlorophenyl sulphoxide (IV) with EtS^- in Pr^nOH at 60° for 2 days afforded in 80% yield the products (VIIIa and b) of β-substitution, as a diastereoisomeric mixture. The corresponding chloro-sulphoxide (III), under the same conditions, gave after 14 days a mixture of (VIIIa and VIIIb) (33%) and the *p*-ethylthiophenyl sulphoxide (IX) (15%), *i.e.* the product of aromatic nucleophilic substitution, together with starting material.

Kinetics Experiments.—The rates of reaction of α-halogeno-sulphoxides (II)—(IV) with Pr^nO^- in Pr^nOH at 80° follow second-order kinetics up to at least 80% conversion. The data are reported in Table 1 together

TABLE 1

Rate coefficients for the reactions of various α-halogeno-sulphoxides (0.03—0.15M) with Pr^nO^- (0.05—0.3M) in Pr^nOH at 80°

Substrate	10^4k [a]/l mol^{-1} s^{-1}
(XII)	7.0 [b]
(Ia)	2.6
(Ib)	2.6
(XI)	0.90
(III)	3.7
(XIII)	76.1 [b]
(IIa)	73.5
(IV)	74.3

[a] Median value of at least two runs. [b] Data from ref. 1.

with the rates of the corresponding reactions of the chloromethyl (XII) and bromomethyl sulphoxide (XIII). Comparison of the rates of reactions of compound (Ia) and of its deuteriated analogue (XI) show a kinetic isotope effect with $k_H/k_D = 2.9$.

Reactions of diastereoisomeric 1-chloroethyl *p*-chlorophenyl sulphoxides (Ia and b) with EtS^- in Pr^nOH follow second-order kinetics up to nearly 20% conversion, $k_{(Ia)}/k_{(Ib)}$ being *ca.* 5. For higher conversions the second-order kinetic plot of diastereoisomer (Ia) shows downward curvature whereas that of its epimer (Ib) shows upward curvature. Such behaviour could be due to the fact that under the reaction conditions the rate of epimerization of (Ia and b) is faster than the rate of substitution. The same phenomenon, although less pronounced, was observed in the reaction of (IIa) with EtS^- in Pr^nOH, a second-order linear plot being observed

TABLE 2

Rate coefficients for the reactions of various α-halogeno-sulphoxides (0.02—0.08M) with EtS^- (0.04—0.15M) in Pr^nOH

Substrate	t/°C	10^4k [a]/l mol^{-1} s^{-1}
(XII)	50	546 [b]
(Ia)	50	0.99 [c]
(Ib)	50	0.21 [c]
(XIII)	40	8 640
(IIa)	40	16.0 [d]

[a] Median value of at least two runs. [b] Data from ref. 1. [c] Rate constant determined for 20% conversion. [d] Rate constant determined for 35% conversion.

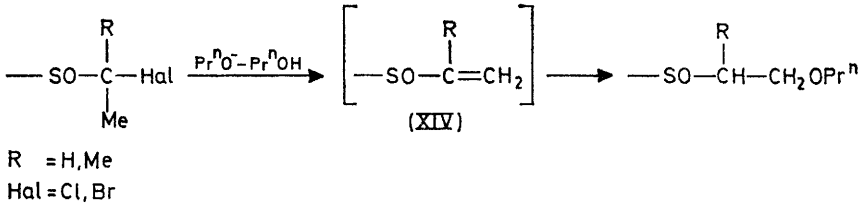
up to 35% conversion. The rate constants are reported in Table 2 together with those of the halogenomethyl derivatives (XII) and (XIII).

DISCUSSION

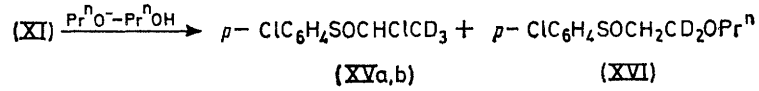
The experimental results indicate that the mechanism of reaction of α-halogeno-sulphoxides (I)—(IV) with Pr^nO^- and EtS^- depends on the structure of the alkyl chain bearing the halogen and on the nature of the nucleophile. Variation of the leaving group does not produce a different mechanism, as previously found [1] for α-halogenomethyl sulphoxides. These latter react with Pr^nO^- *via* S_N2 displacement.[1]

The experimental data indicate that 1-halogenoethyl and -1-methylethyl derivatives react with the strongly basic Pr^nO^- to give the products of β-substitution, probably *via* elimination–addition (Scheme 1). It was not possible to detect the intermediacy of the vinyl sulphoxides (XIV); however it is known [10] that they easily add alcohols in the presence of alcoholates. H/D Exchange tests were performed by quenching the reaction of (XI) with Pr^nO^- at 50% conversion (Scheme 2).

Starting from diastereoisomerically pure (XI) a



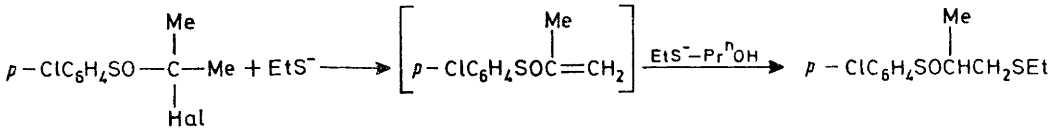
SCHEME 1



SCHEME 2

mixture of the diastereoisomeric *p*-chlorophenyl 1-chloro-2,2,2-trideuterioethyl sulphoxides (XVa and b) and 2-(*p*-chlorophenylsulphinyl)-1,1-dideuterioethyl propyl ether (XVI) was obtained. Therefore complete exchange at α-carbon but no exchange at β-carbon occurs. In agreement with an elimination–addition process, the reactivity of 1-halogeno-ethyl and -1-methylethyl sulphoxides having the same leaving group are similar (see Table 1). The kinetic isotope effect (k_H/k_D 2.9) measured for (Ia) and (XI), is in agreement with a concerted process.*

In the reaction of 1-halogeno-ethyl and -1-methylethyl sulphoxides (I)—(IV) with EtS^-, both direct substitution and elimination–addition are disfavoured, the former by steric hindrance, the latter by the low basicity of the nucleophile. α-Halogenoethyl sulphoxides (I) and (II) react with EtS^- to give the α-substitution products *via* S_N2 displacement, and, as expected, the rate of reaction is much lower than that of the corresponding α-halogenomethyl derivatives (XII) and (XIII) (see Table 2). In agreement with an S_N2 mechanism is the different reactivity toward EtS^- of the diastereoisomers (Ia and b),† whereas they have the same reactivity in the elimination–addition process promoted by Pr^nO^-.



(III),(IV) (XV) (VIIIa,b)

SCHEME 3

In the isopropyl derivatives (III) and (IV) due to the increased steric hindrance to direct nucleophilic displacement, the reaction with EtS^- gives the β-substitution products (VIIIa and b), probably *via* elimination–addition (Scheme 3). The formation of intermediate (XIV) should occur by a concerted process, since the formation of a carbocation is highly inhibited owing to the electron-withdrawing effect of the SO group. In view of the fact that the sulphinyl group poorly activates nucleophilic aromatic substitution,[14] the occurrence of a substantial amount of (IX) in the reaction mixture starting from (III) is clear evidence that aliphatic nucleophilic substitution in 1-halogeno-1-methylethyl sulphoxides is a very disfavoured process.

EXPERIMENTAL

^1H N.m.r. spectra were recorded with a Varian A 60 spectrometer ($CDCl_3$ as solvent and tetramethylsilane as internal standard). Mass spectra were taken with an RMV Hitachi 6 D mass spectrometer.

Materials and Solvents.—n-Propanol and ethanethiol were AnalaR grade commercial products, purified, when necessary, by standard methods.

α-Halogeno-sulphoxides.—Compounds (Ia), (IIa), (III), and (IV) were prepared by α-halogenation of the corresponding sulphoxides or sulphides with (dichloroiodo)-benzene or bromine and silver nitrate in the presence of pyridine, as previously described.[10] They were carefully purified by column chromatography (silica gel; eluant light petroleum–ether 2 : 1) and/or by crystallisation. 1-*Chloroethyl* p-*chlorophenyl sulphoxide* (Ib) was obtained by inversion of its epimer (Ia) with triethyloxonium fluoroborate according to Johnson.[11] Physical properties, yields, and analytical data are reported in Table 3 and spectra data in Table 4.

1-*Chloro*-1,2,2,2-*tetradeuterioethyl* p-*Chlorophenyl Sulphoxide* (XI).—Pentadeuterioethyl toluene-*p*-sulphonate (XVII), m.p. 32—34°, isotopically pure by ^1H n.m.r., was prepared by reaction of toluene-*p*-sulphonyl chloride with perdeuterioethanol as previously described [15] for the isotopically normal derivative (lit.,[15] m.p. 33—34°). Re-

TABLE 3

Physical properties and analyses of halogenosulphoxides

Substrate	M.p. (°C)	Yield (%)	Formula	Found (%) C	Found (%) H	Required (%) C	Required (%) H
(Ia)	58—60 [a]	65	$C_8H_8Cl_2OS$	42.9	3.7	43.05	3.6
(Ib)	53—54 [a]	52	$C_8H_8Cl_2OS$	42.95	3.65	43.05	3.6
(IIa)	81—82 [a]	45	$C_8H_8BrClOS$	36.0	3.0	35.9	3.0
(III)	42—43 [b]	75					
(IV)	Oil [c]	48					

[a] From n-hexane–benzene (4 : 1). [b] Lit.,[11] m.p. 42—43°. [c] Characterized through ^1H n.m.r. and oxidation to the corresponding sulphone, m.p. 101—102° (from 95% EtOH) (Found, C, 36.45; H, 3.45. $C_9H_{10}BrClO_2S$ requires C, 36.3; H, 3.4%).

* This value is lower than that normally found [12] for an *E*2 mechanism; however it must be pointed out that this was determined at 80° and it is well known that isotope effects are temperature dependent.[13]

† Similar results were observed on qualitative grounds by Tsuchihashi [8] for the reaction of *cis*- and *trans*-2-chlorothiolan 1-oxides with MeS^-.

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action of the ester (0.1 mol) with potassium *p*-chlorobenzenethiolate (0.11 mol) in anhydrous acetone (50 ml) at reflux for 15 h under nitrogen afforded *p*-chlorophenyl pentadeuterioethyl sulphide (XVIII), n_D^{20} 1.5803, b.p. 121—123° at 18 mmHg (lit.,[16] n_D^{20} 1.5800, b.p. 123° at 18 mmHg, for the corresponding isotopically normal sulphide). The *α-halogeno-sulphoxide* (XI) was obtained from the sulphide in 51% yield, m.p. 58—59° (from n-hexane–benzene 4 : 1). A mixture of (XI) with (Ia) showed no m.p. depression. Compound (XI) was isotopically pure by ^{1}H n.m.r.

Reaction Products from 1-*Halogenoethyl* (I) *and* (II), *and* 1-*Halogeno*-1-*methylethyl Sulphoxides* (III) *and* (IV) *with Sodium n-Propoxide.*—(a) *From* 1-*chloroethyl* p-*chlorophenyl sulphoxides* (Ia *and* b). To a solution of (Ia) (1.12 g, 5 mmol) in Pr^{n}OH (20 ml) a 0.5M solution of Pr^{n}ONa in Pr^{n}OH (12 ml) was added rapidly with stirring and heated at 80° for 31 h. The reaction mixture was diluted with methylene chloride (60 ml), quenched by adding aqueous 10% hydrochloric acid, and the organic layer was separated, washed with water, and dried (Na_2SO_4). Evaporation of the solvent afforded the crude product which was separated by column chromatography [silica gel; ether–light petroleum (1 : 3)] to give epimeric chloro-sulphoxides (Ia and b) (0.15 g) and 2-(p-*chlorophenylsulphinyl*)*ethyl propyl ether* (V) (1.0 g, 81%), n_D^{19} 1.5431 (Found: C, 53.45; H, 6.15. $C_{11}H_{15}ClO_2S$ requires C, 53.55; H, 6.15%). The same results were obtained starting from (Ib).

(b) *From* 1-*bromoethyl* p-*chlorophenyl sulphoxide* (IIa). Under the same conditions as in (a), after 17 h bromosulphoxide (IIa) (4.02 g, 15 mmol) gave epimeric α-bromosulphoxides (IIa and b) (0.45 g) and (V) (2.75 g, 77%.) The mixture of (IIa and b) was separated into the components by column chromatography [silica gel; ether–light petroleum (1 : 4)]. Compounds (IIa and b) were separately oxidised with *m*-chloroperbenzoic acid to give quantitatively 1-*bromoethyl* p-*chlorophenyl sulphone* (XIX), m.p. 85—86° (from 95% EtOH) (Found: C, 33.95; H, 2.8. $C_8H_8BrClO_2S$ requires C, 33.9; H, 2.85%).

(c) *From* 1-*chloro*-1-*methylethyl* p-*chlorophenyl sulphoxide* (III). α-Chloro-sulphoxide (III) (2.37 g, 10 mmol) reacted under the same conditions as in (a) for 40 h to give after column chromatography [silica gel; ether–light petroleum (1 : 4)] starting sulphoxide (III) (0.24 g), 2-(p-*chlorophenylsulphinyl*)*propyl propyl ether* (VIa) (1.1 g), n_D^{20} 1.5362, and the epimer (VIb) (0.96 g), n_D^{20} 1.5404 (overall yield 78%). Oxidation of (VIa and b) with *m*-chloroperbenzoic acid afforded in quantitative yield 2-(p-*chlorophenylsulphonyl*)*propyl propyl ether* (XX), n_D^{16} 1.5271 (Found: C, 52.3; H, 6.2. $C_{12}H_{17}ClO_3S$ requires C, 52.1; H, 6.2%).

(d) *From* 1-*bromo*-1-*methylethyl* p-*chlorophenyl sulphoxide* (IV). Under the same conditions as in (a) bromo-sulphoxide (IV) (2.82 g, 10 mmol) after 18 h gave (VIa and b)

TABLE 4

^{1}H N.m.r. data

Compound	δ ($CDCl_3$)
(Ia)	7.42—7.77 (4 H, m, Ar), 4.73 (1 H, q, SOCH), 1.62 (3 H, d, Me)
(Ib)	7.38—7.76 (4 H, m, Ar), 4.48 (1 H, q, SOCH), 1.77 (3 H, d, Me)
(IIa)	7.43—7.78 (4 H, m, Ar), 4.75 (1 H, q, SOCH), 1.82 (3 H, d, Me)
(IIb)	7.42—7.79 (4 H, m, Ar), 4.57 (1 H, q, SOCH), 1.93 (3 H, d, Me)
(III)	7.40—7.80 (4 H, m, Ar), 1.71 (6 H, d, 2 × Me)
(IV)	7.38—7.78 (4 H, m, Ar), 1.88 (6 H, d, 2 × Me)
(V)	7.38—7.71 (4 H, m, Ar), 3.73 (2 H, t, CH_2OCH_2), 3.44 (2 H, t, CH_2OCH_2), 2.98 (2 H, t, $SOCH_2$), 1.53 (2 H, m, CH_2Me), 0.93 (3 H, t, Me)
(VIa)	7.37—7.67 (4 H, m, Ar), 3.68 (2 H, d, $CHCH_2$), 3.47 (2 H, t, CH_2OCH_2), 2.83 (1 H, m, SOCH), 1.52 (2 H, m, CH_2Me), 1.00 (3 H, d, CHMe), 0.93 (3 H, t, CH_2Me)
(VIb)	7.38—7.72 (4 H, m, Ar), 3.56 (2 H, d, $CHCH_2$), 3.40 (2 H, t, CH_2OCH_2), 3.07 (1 H, m, SOCH), 1.57 (2 H, m, CH_2Me), 1.11 (2 H, d, CHMe), 0.92 (3 H, t, CH_2Me)
(VIIa)	7.40—7.76 (4 H, m, Ar), 3.62 (1 H, q, SOCH), 2.55 (2 H, q, CH_2Me), 1.48 (3 H, d, CHMe), 1.21 (3 H, t, CH_2Me)
(VIIb)	7.39—7.80 (4 H, m, Ar), 3.90 (1 H, q, SOCH), 2.80 (2 H, q, CH_2Me), 1.28 (3 H, d, CHMe), 1.30 (3 H, t, CH_2Me)
(VIIIa)	7.46—7.57 (4 H, m, Ar), 2.30—3.00 (5 H, m, $SOCHCH_2SCH_2$), 1.08—1.45 (6 H, m, 2 × Me)
(VIIIb)	7.49—7.61 (4 H, m, Ar), 2.40—3.10 (5 H, m, $SOCHCH_2SCH_2$), 1.10—1.47 (6 H, m, 2 × Me)
(IX)	7.30—7.70 (4 H, m, Ar), 3.01 (2 H, q, CH_2Me), 1.72 (6 H, d, 2 × Me), 1.36 (3 H, t, CH_2Me)
(X)	8.08—8.38 (4 H, m, Ar), 3.22 (2 H, q, CH_2Me), 1.93 (6 H, s, 2 × Me), 1.33 (3 H, t, CH_2Me)
(XVa)	7.42—7.77 (4 H, m, Ar), 4.73 (1 H, s, SOCH)
(XVb)	7.38—7.76 (4 H, m, Ar), 4.48 (1 H, s, SOCH)
(XVI)	7.39—7.73 (4 H, m, Ar), 3.44 (2 H, t, CD_2OCH_2), 2.98 (2 H, s, $SOCH_2$), 1.53 (2 H, m, CH_2Me), 0.93 (3 H, t, Me)
(XX)	7.43—7.92 (4 H, m, Ar), 3.18—3.82 (5 H, m, $SO_2CHCH_2OCH_2$), 1.17—1.62 (5 H, m, CH_2Me, CHMe), 0.80 (3 H, t, CH_2Me)
(XXI)	7.47—7.98 (4 H, m, Ar), 4.38 (1 H, q, SO_2CH), 3.56 (2 H, q, CH_2Me), 1.70 (3 H, d, CHMe), 1.48 (3 H, t, CH_2Me)

(1.9 g, 76%) in *ca.* 1 : 1 ratio (by ^{1}H n.m.r.) together with starting material (0.52 g).

Reaction Products from 1-*Halogenoethyl* (I) *and* (II), *and* 1-*Halogeno*-1-*methylethyl Sulphoxides* (III) *and* (IV) *with Sodium Ethanethiolate in* Pr^{n}OH.—(a) *From* 1-*chloroethyl sulphoxide* (Ia). To a solution of α-chlorosulphoxide (Ia) (2.23 g, 10 mmol) in Pr^{n}OH (20 ml) a 0.54M solution of sodium ethane thiolate in Pr^{n}OH (28 mmol) was rapidly added with stirring and heated at 60° for 40 h. Work-up as described above for the reaction with Pr^{n}O$^-$, gave after column chromatography [silica gel; ether–light petroleum (1 : 4)] an almost equimolecular mixture (by ^{1}H n.m.r.) of diastereoisomeric chloro-sulphoxides (Ia and b) (0.26 g), 1-(p-*chlorophenylsulphinyl*)*ethyl ethyl sulphide* (VIIa) (0.54 g), a mixture of (VIIa and b) (0.88 g) in *ca.* 1 : 1 ratio (by ^{1}H n.m.r.), and sulphoxide (VIIb) (0.58 g). Compounds (VIIa and b) as well as a mixture of (VIIa and b) were separately oxidised with *m*-chloroperbenzoic acid to give the same 1-(p-*chlorophenylsulphonyl*)*ethyl ethyl sulphone* (XXI) in 90% yield, m.p. 108—109° (from 95% EtOH) (Found: C, 40.35; H, 4.5. $C_{10}H_{13}ClO_4S_2$ requires C, 40.45; H, 4.4%).

The same results were obtained starting from (Ib).

(b) *From α-bromoethyl sulphoxide* (IIa). Under the same

[16] M. Kulka, *Canad. J. Chem.*, 1958, **36**, 150.

conditions as in (a) after 15 h bromo-sulphoxide (IIa) (2.67 g, 10 mmol) gave epimeric α-bromo-sulphoxides (IIa and b) (0.21 g), compound (VIIa) (0.80 g), a mixture of (VIIa and b) (0.75 g) in 1 : 1 ratio, and compound (VIIb) (0.79 g) (overall yield 92%).

(c) *From* 1-*chloro*-1-*methylethyl sulphoxide* (III). Chloro-sulphoxide (III) (2.37 g, 10 mol) reacted under the same conditions as in (a) for 14 days to give after column chromatography [silica gel; ether–light petroleum (1 : 4)] starting sulphoxide (III) (1.02 g), 2-(p-*chlorophenylsulphinyl*)-*ethyl propyl sulphide* as a mixture of diastereoisomers (VIIIa and b) (0.86 g, 33%), and 1-*chloro*-1-*methylethyl* p-*ethylthiophenyl sulphoxide* (IX) (0.28 g, 15%), as an oil. A mixture of (VIIIa and b) was separated into the components by column chromatography [silica gel; ether–light petroleum (1 : 4)]. Compounds (VIIIa and b) were separately oxidised to afford quantitatively 2-(p-*chlorophenylsulphonyl*)*ethyl propyl sulphone*, m.p. 124—125° (from 95% EtOH) (Found: C, 42.6; H, 4.85. $C_{11}H_{15}ClO_4S_2$ requires C, 42.5; H, 4.85%). Compound (IX) was identified by its ^{1}H n.m.r. spectrum and oxidation to the corresponding 1-*chloro*-1-*methylethyl* p-*ethylsulphonylphenyl sulphone* (X), m.p. 165—166° (from 95% EtOH) (Found: C, 42.3; H, 4.85. $C_{11}H_{15}ClO_4S_2$ requires C, 42.50; H, 4.85%); *m/e* 311 (M^+), 234 (*p*-$EtSO_2C_6H_4SO_2H$), 170 ($EtSO_2Ph$), and 78 (Me_2CHCl).

(d) *From* 1-*bromo*-1-*methylethyl sulphoxide* (IV). Under the same conditions as in (a) after 46 h bromo-sulphoxide (IV) (2.82 g, 10 mmol) gave, after column chromatography [silica gel; ether–light petroleum (1 : 4)] starting sulphoxide (0.26 g) together with a 1 : 1 mixture (^{1}H n.m.r.) of diastereoisomers (VIIIa and b) (2 g, 78%), identified as described in (c).

Hydrogen–Deuterium Exchange in the Reaction of p-*Chlorophenyl* 1-*Chloro*-1,2,2,2-*tetradeuterioethyl Sulphoxide* (XI) *and Sodium n-Propoxide in n-Propanol*.—Chloro-sulphoxide (XI) (1.13 g, 5 mmol) and 0.1M-sodium n-propoxide in n-propanol (75 ml) were reacted in conditions similar to those of the kinetic experiments. The reaction was stopped at 50% conversion by acidification with 10% aqueous hydrochloric acid. The usual work up afforded *p*-chlorophenyl 1-chloro-2,2,2-trideuterioethyl sulphoxides (XVa and b) (0.55 g, 48%), as an oil (identified by ^{1}H n.m.r. and t.l.c. and 2-(*p*-chlorophenylsulphinyl)-1,1-dideuterioethyl propyl ether (XVI) (identified by ^{1}H n.m.r.).

Epimerization of Sulphoxide (Ia *and* b), (IIa), (VIIa *and* b).—Sulphoxides (Ia and b) and (IIa) were reacted with EtS^- under conditions similar to those of the kinetic experiments. The reaction was stopped after 30% conversion and worked up as described above. An equimolecular mixture (by ^{1}H n.m.r.) of epimeric sulphoxides (Ia and b) and (IIa and b), was recovered. The sulphoxides (VIIa and b) were separately reacted with EtS^- under the same conditions. The reaction was quenched after 1 h and the usual work up afforded in both cases a nearly equimolar mixture of the diastereoisomers (VIIa and b) (^{1}H n.m.r. analysis).

Kinetic Measurements.—Aliquot portions of the reacting solutions were withdrawn at intervals and quenched by adding a known amount of standard hydrochloric acid, the excess of which was then determined with sodium hydroxide solution (phenolphthalein in the case of Pr^nO^- and Bromocresol Green in the case of EtS^-). The rate constants were obtained by plotting $\log(a - x)/(b - x)$ against time.

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