Conformational Control in Eliminations with the $(E_1cB)_R$ Mechanism

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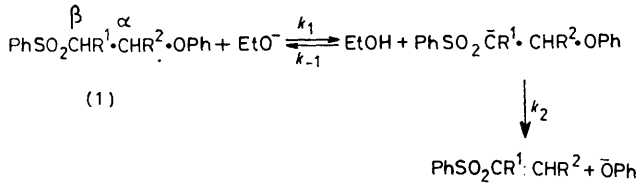
Summary For alkene-forming elimination of phenoxide ion from sulphonyl-stabilised carbanions, stereospecificity depends on the configuration of the carbanion and the population of its conformers.

EARLIER work[1,2] has shown that elimination of phenoxide ion from 2-phenoxyethylphenyl sulphones (**1**; $R^1 = R^2 = H$) in ethanolic sodium ethoxide occurs by the $(E_1cB)_R$ mechanism.

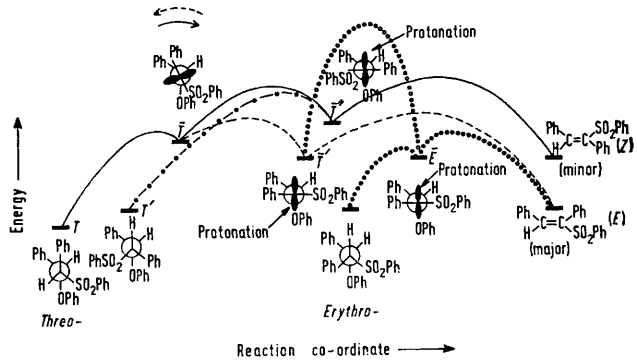
We now report on reactions with the *erythro*- and *threo*-isomers of 1,2-diphenyl-2-phenoxyethyl phenyl sulphone (**1**; $R^1 = R^2 = Ph$). Rates of elimination are compared (Table) with those of the unsubstituted compound and the α- and β-monophenyl[2] derivatives. It has been confirmed that the minor (*Z*) product obtained from the *threo*-isomer is not converted into the thermodynamically more stable *E*-isomer under the reaction conditions. There is no interconversion of the *erythro*- and the *threo*-isomers. ^1H N.m.r. examination of the products of partial reactions with each isomer showed no formation of the other isomer under conditions in which 0·5% would easily have been detected. We assign the $(E_1cB)_R$ mechanism to all reactions on the evidence of the recovery of deuteriated starting material from reactions in EtOD and the fact that detritiation rate constants substantially exceed elimination rate constants (Scheme 1).



SCHEME 1

We suggest that the products of these reactions and their relative rates are under conformational control. Preferred ground state conformations of the two isomers (Scheme 2) are assigned[3] from average ^1H n.m.r. coupling constants, $J(H_\alpha\text{-}H_\beta)$ (*erythro*, 3; *threo*, 9 Hz). Removal of a proton gives a planar carbanion.[4]

For elimination of phenoxide ion to occur, the preferred orientation of the *p*-orbital of the carbanion and of the C–O bond is periplanar[5] (ions $\overline{E}$ and $\overline{T}'$ and $\overline{T}''$) (Scheme 2). The



SCHEME 2

appropriate conformation is directly achieved for the *erythro*-isomer by removal of the β-proton and the ion formed is the more stable of the two alternatives as the phenyl–phenylsulphonyl interaction is avoided. For the *threo*-isomer, the preferential ground-state conformation is of lower energy, but the anion directly formed ($\overline{T}$) does not have the required periplanar arrangement. Rotation to achieve this arrangement can occur in either direction. Clockwise rotation gives ion $\overline{T}''$, the conformation of higher energy and lower population which leads to the minor product. Anti-clockwise rotation gives the ion $\overline{T}'$, which is a C–S rotamer of ion $\overline{E}$, protonation of each of these ions being stereospecific and returning the ion to the original starting material.[4] The ions are separated by an energy barrier which is higher than that for reaction of either ion to give elimination or reprotonation.

The data on relative rates of elimination and detritiation are consistent with this view. An α-phenyl substituent has little effect on rate, while a β-phenyl substituent causes acceleration. This acceleration is not as large as would be expected from the effect of the group on the dissociation of the β-C–H bond[6] and we attribute this to the operation of

TABLE
Elimination of phenoxide ion from 2-phenoxyethyl phenyl sulphones

Substrate (**1**)		k_{rel}^{obs}[a]	k_{rel}^{detrit}[a]	$k_2 : k_{-1}$ (rel)	Product	Yield/%
R^1	R^2					
H	H	1(0·35)	1(6·3)	1	$PhSO_2{\cdot}CH_2CH_2OEt$	99
Ph	H	64	1·3	49	$PhSO_2CHPh{\cdot}CH_2OEt$	91
H	Ph	1·3	0·2	6·5	$PhSO_2CH_2CHPhOEt$	97
Ph	Ph (*erythro*)	3	2·2	1·4	$PhSO_2C(Ph):CHPh$ (*E*)	98
Ph	Ph (*threo*)	0·05	0·0051	10	$PhSO_2C(Ph):CHPh$ (*E*)	71
					,, (*Z*)	21

[a] Figure in parentheses represents absolute value of *k* (l mol^{-1} s^{-1} at 25 °C).

adverse steric effects in the planar ion. With both α- and β-phenyl groups present, the energies of the carbanions are raised because of steric interaction between the substituents. For the less stable *erythro*-isomer, the rate of formation of the carbanion is rather similar to that in the unsubstituted and β-phenyl compounds but expulsion of the leaving group (reflected in the ratio of $k_2 : k_{-1}$ if it is assumed that reprotonation of the carbon is very rapid[7]) is very much slower than for the β-phenyl compound. For the *threo*-isomer, detritiation is very much slower than for the *erythro*-isomer. The ground state energy is lower than that of the *erythro*-isomer and the energy of the initially produced ion, $\overline{T}$, is higher. Expulsion of the leaving group, however, occurs more readily in the ions derived from the *threo*-isomer.

Cristol[8] and Naso[9] have examined similar reactions of the related chlorides $PhSO_2{\cdot}CHR^1{\cdot}CHR^2{\cdot}Cl$ ($R^1 = R^2 = Ph$). The reactions show primary deuterium isotope effects[9] and possibly have the $(E_1cB)_I$ mechanism. This is suggested by the similarity of the k_{obs} ratio ($E : T = 105 : 1$) to the detritiation ratio (430 : 1) obtained for the phenyl ethers in this work. Cristol and Pappas[8] discussed their product distribution (92% of *Z*-alkene from the *erythro*-isomer and 84% from the *threo*-isomer) in terms of 'stereoconvergency.' It seems likely that the 'stereoconvergency' is the result of conformation control as described above. By contrast, Bordwell and Landis[10] find a much smaller rate differential ($E : T = 2{\cdot}3 : 1$) between the diastereoisomeric *p*-bromobenzenesulphonates, $p\text{-}MeC_6H_4SO_2CHMe.CHMe.SO_3C_6H_4\text{-}Br\text{-}p$ and elimination in each diastereoisomer was stereospecifically (>95%) *anti*. These reactions probably also have the $(E_1cB)_I$ mechanism.[11] Since the carbanion is pyramidal and conformational energy differences are lower, eclipsing of substituents can be avoided and *anti*-elimination occurs.

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