The Nature of the α-Sulphinyl Carbanion Derived from Methyl 1-Phenylethyl Sulphoxide

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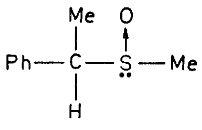
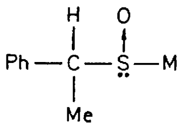
Summary For hydroxide-ion-catalysed proton removal from methyl 1-phenylethyl sulphoxide $k_{ex}/k_{ep} = 1{\cdot}30$ (ex refers to exchange and ep to epimerization), a result consistent with the intervention of either two rapidly inverting pyramidal anions or a single planar anion.

The diastereotopic protons of benzyl methyl sulphoxide display a remarkable difference in kinetic acidities.[1-4] Although some previous work has been interpreted in terms of two ions which are reprotonated faster than they equilibrate,[2] experiments have so far not allowed discrimination between processes involving planar or rapidly inverting carbanions as opposed to those involving slowly inverting or non-inverting carbanions. In order to gain insight into the nature of the intermediates and thus into the origin of the kinetic preference, we have determined the rates of exchange and of epimerization[5] of the closely related methyl 1-phenylethyl sulphoxide.

The kinetics of isotopic exchange and of epimerization of the diastereoisomers (*R*,*S*/*S*,*R*)-1-phenylethyl methyl sulphoxide (I) {contaminated with 5% of (*S*,*S*/*R*,*R*) (II)} were determined in 0·74M-NaOD–D_2O at 56°. Samples were analysed by n.m.r. for deuterium uptake and extent of epimerization. The equilibrium constant for the diastereoisomers $\{K_{eq} = [(II)]/[(I)]\}$ was determined to be 2·0; both exchange and epimerization gave good pseudo-first-order kinetics with $k^{I}_{ex} = 6{\cdot}89 \times 10^{-5}\ s^{-1}$, $k^{I}_{ep} = 5{\cdot}31 \times 10^{-5}\ s^{-1}$ and $k^{I}_{ex}/k^{I}_{ep} = 1{\cdot}30$. By monitoring the rate of deuterium uptake of an equilibrium mixture of diastereoisomers in 0·53M-NaOD–D_2O by n.m.r. and analysing the composite rate data,[6] the rate ratio, k^{II}_{ex}/k^{I}_{ex}, was determined as 8·6. The rate ratio for benzyl methyl sulphoxide is reported[1,2] to be 13—14.


(*R*,*S*) (I)


(*S*,*S*) (II)

These observations require a mechanism in which any anionic intermediates which intervene are interconverted rapidly relative to the rate of reprotonation, since even an interconversion rate equal to the reprotonation rate requires $k^{I}_{ex}/k^{I}_{ep} \approx 2$. In fact, within experimental error, the intermediate anionic species may well be planar. If we assume that the interconversion rates of the anions are solvent-independent, the results of our experiments on the methyl phenylethyl sulphoxide system are at variance with previous implications for the benzyl methyl sulphoxide system that quenching of monoanions is rapid relative to interconversion, and thus that the product ratios are indicative of anion stability.

The differential kinetic acidities of the diastereotopic protons in benzyl methyl sulphoxide have previously been shown to depend on the nature of the base and of the solvent system,[2] indicating that deprotonation and protonation rates are not solely intrinsic properties of the isolated sulphoxide and its conjugate base. More specifically, since the intermediate anions are either planar or interconverting rapidly, the transition states for proton removal do not simply reflect the intrinsic relative stabilities of such anion(s). We have now demonstrated this not only by the above experiments, but also by confirming[4a] that deprotonation by n-butyl-lithium in tetrahydrofuran followed by quenching in D_2O (all at −70°) occurs with predominant overall inversion. Thus two successive treatments of benzyl methyl sulphoxide produced [$^2H_2$]-compound essentially quantitatively. That this was not simply due to a deuterium isotope effect was demonstrated by subjecting the diastereomeric [$^2H_1$]benzyl methyl sulphoxide, obtained from exchange in D_2O, to the same conditions and recovering [$^2H_1$]-compound of inverted configuration. Consequently under these conditions the proton is preferentially removed from one position and preferentially inserted in the other. This clearly results from the change in conditions, since such a process would violate microscopic reversibility in an equilibrium situation.

Added in proof: K. Nishihata and M. Nishio (*J.C.S. Perkin II*, 1972, 1730) and R. Viau and T. Durst (*J. Amer. Chem. Soc.*, 1973, **95**, 1346) have recently reported similar quenching studies. Our results are in qualitative agreement with those of Nishihata and Nishio, the *pro-R* hydrogen in (*S*)-benzyl methyl sulphoxide being the more reactive toward butyl-lithium in THF.

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