Stereoselectivity in the Allyl Sulphenate–Sulphoxide Rearrangement

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Summary *cis*- and *trans*-But-2-enyl toluene-*p*-sulphenates rearrange stereoselectively, in accord with a [2,3]-sigmatropic mechanism.

I have recently observed stereoselectivity in the Wittig rearrangement of an allyl ether,[1] which can be explained in terms of a [2,3]-sigmatropic mechanism[2] with an *exo*-transition state preferred over an *endo*-one. The reversible allyl sulphenate–sulphoxide rearrangement, discovered and studied by Bickart, Carson, Jakobus, Miller, and Mislow[3] can be considered as a [2,3]-sigmatropic change[4] and is stereoselective.[3] In order to understand further the stereochemistry of [2,3]-sigmatropic changes, I have re-examined the rearrangement of but-2-enyl toluene-*p*-sulphenates (I).

A four-centre transition state in the rearrangement of *trans*-but-2-enyl toluene-*p*-sulphenate (*trans*-I) to α-methylallyl toluene-*p*-sulphoxides (IIa) and (IIb) can be viewed as a toluene-*p*-sulphinyl radical interacting with a *trans*-but-2-enyl radical. This four-centre interaction can occur in a variety of geometrical arrangements.[3] All such transition states can be divided into two groups which are diastereomeric with respect to each other, namely *exo*-transition states, which lead to diastereomer (IIa) and *endo*-ones, which lead to diastereomer (IIb). In the rearrangement of *cis*-but-2-enyl toluene-*p*-sulphenate (*cis*-I), *exo*-transition states lead to (IIb) and *endo*-ones to (IIa).

exo-Transition states are expected to be favoured over *endo*-ones for steric reasons and possibly because of symmetry-controlled (anti-bonding) secondary orbital interactions. Accordingly, under conditions of kinetic control, (*trans*-I) should rearrange preferentially to diastereomer (IIa) and (*cis*-I) preferentially to (IIb).

When lithium *trans*-but-2-enyl alcoholate (94% *trans*, 6% *cis*) was treated with toluene-*p*-sulphenyl chloride in ether–hexane at −75°,[3] the cold mixture poured into water of 22°, rapidly (15—20 min) worked-up at room temperature (22°), and the crude product immediately examined by n.m.r. spectroscopy,† a *ca.* 76 : 24 mixture of diastereomers (II) was observed‡ to be present. The same procedure, using lithium *cis*-but-2-enyl alcoholate (97% *cis*, 3% *trans*)

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† Varian A-60, 0·65 M-solutions in CCl_4.

‡ The sharp methyl doublets of (IIa) and (IIb) (ref. 3) have different (*ca.* 0·07 p.p.m.)† chemical shifts. This difference varies with concentration and solvent.

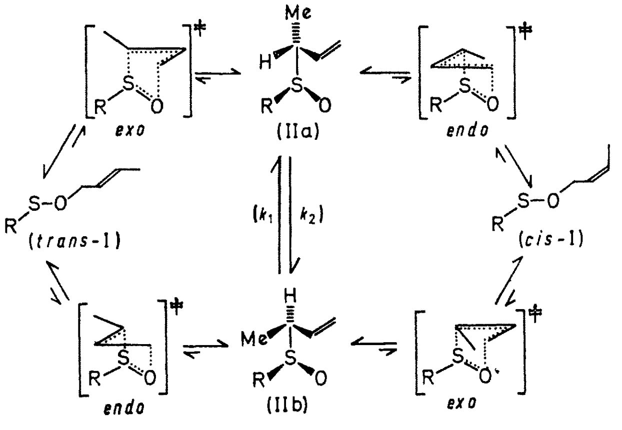
was observed to give a *ca.* 22 : 78 mixture of diastereomers (II).

On being monitored by n.m.r.,† both mixtures were observed to equilibrate to a *ca.* 52 : 48 mixture with a rate constant $(k_1 + k_2)$ of *ca.* $2{\cdot}5 \times 10^{-4}\,s^{-1}$ at +22°.

The but-2-enyl sulphenates (II) can be assumed to be stable at −75°[3] and essentially to rearrange at +22°. I estimate their half-lives at this temperature to be of the order of 10 s or less. The half-life of epimerisation is *ca.* 2 h. Accordingly, extrapolation of the epimerisation process back to the time t_0 of pouring the cold (−75°) solutions into water at 22° leads to a product distribution which is close to being kinetically controlled.

Since $(k_1 + k_2)$ is strongly dependent on solvent polarity,[3] its overall value during work-up was estimated by dissolving the initially obtained mixture from lithium *trans*-but-2-enyl alcoholate in ether–hexane containing lithium chloride at room temperature and then working-up and analysing this mixture as before. Using the constant (*ca.* $1{\cdot}9 \times 10^{-4}\,s^{-1}$) so obtained for extrapolation to t_0 at 22°, it could be estimated that the kinetically-controlled rearrangements lead to a *ca.* 83 : 17 mixture of diastereomers (II) in the *trans*-but-2-enyl case and to a *ca.* 17 : 83 mixture in the *cis*-but-2-enyl case. On correcting for isomer impurities in the but-2-enyl alcohol samples used, this corresponds to *ca.* 74 and *ca.* 72% stereoselectivity and to a difference of ΔF_{exo} and ΔF_{endo} of *ca.* 1 kcal/mole (+22°).

The observation,[3] that optically active α-methylallyl toluene-*p*-sulphenate (III) rearranges to optically active *trans*-but-2-enyl toluene-*p*-sulphoxide (*trans*-IV) with at least 37% stereoselectivity can also be explained in terms of preferred *exo*-transition states.



R = p-MeC$_6$H$_4$: in each case only one enantiomer is drawn.

Preferential formation of (*trans*-IV) rather than the *cis*-isomer (*cis*-IV)[3] implies that folding of the molecule towards *exo*- or *endo*-transition states occurs preferentially in such a way that the methyl group is in a quasi-equatorial rather than a quasi-axial position. This principle was also noted in Wittig rearrangements of α-methylallyl ethers[1,5,6] and generally in [3,3]-sigmatropic rearrangements.[7]

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[1] V. Rautenstrauch, *Chem. Comm.*, 1970, 4.
[2] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, 1969, **81**, 849; *Angew. Chem. Internat. Edn.*, 1969, **11**, 781.
[3] P. Bickart, F. W. Carson, J. Jakobus, E. G. Miller, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4869.
[4] A. Jefferson and F. Scheinmann, *Quart. Rev.*, 1968, **22**, 391.
[5] U. Schöllkopf and K. Fellenberger, *Annalen*, 1966, **698**, 80.
[6] Y. Makisumi and S. Notzumoto, *Tetrahedron Letters*, 1966, 6393.
[7] C. L. Perrin and D. J. Faulkner, *Tetrahedron Letters*, 1969, 2783, and references therein.