Asymmetric Induction and Racemisation in Allenic Sulphoxides

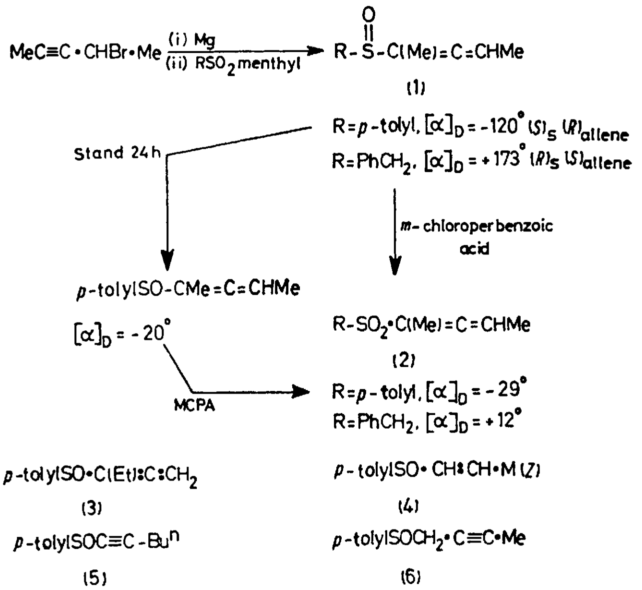
By Mauro Cinquini and Stefano Colonna
(*Universita di Milano, Istituto di Chemica Industriale, Via C. Golgi, 9, 20133, Milano, Italy*)
and Charles J. M. Stirling*
(*School of Physical and Molecular Sciences, University College of North Wales, Bangor*)

Summary Reactions of menthyl esters of sulphinic acids with appropriately substituted propargyl Grignard reagents yield allenic sulphoxides which are asymmetric at sulphur and in the allene system; epimerisation at sulphur in these sulphoxides apparently occurs by sulphoxide–sulphenate equilibration but with preservation of asymmetry in the allene system.

Induction of asymmetry at carbon by an asymmetric sulphur atom[1] and at sulphur by an asymmetric carbon atom[2,3] has been observed in additions to α,β-unsaturated sulphoxides and in the rearrangement of alkenyl and alkynyl sulphenic esters respectively.

We now report induction of chirality in allenic systems under the influence of an asymmetric sulphur atom.

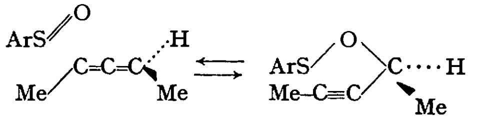
Following Andersen's[4] procedure, successive treatment of 2-bromopent-3-yne with magnesium in tetrahydrofuran and then with menthyl (*R*)-(+)-benzyl- or (*S*)-(−)-toluene-*p*-sulphinates gave the allenic sulphoxides (**1**) together with minor amounts of acetylenic sulphoxides. Oxidation of the sulphoxides with *m*-chloroperbenzoic acid (MCPA) gave the optically active allenic sulphones (**2**) (Scheme). The rotation of the sulphone (**2**; R = *p*-tolyl) indicates, by comparison with a similar sulphone which is about 30% optically pure,[3] that asymmetric induction in the allene system approaches 100%. Application of empirical rules[5] to the rotations of the allenic sulphones suggests that the (*S*)-toluene-*p*-sulphinate gives (*R*)-allene and the (*R*)-benzylsulphinate gives (*S*)-allene.



Scheme

Surprisingly, asymmetric induction in the Andersen synthesis of simple alkyl sulphoxides has not been studied. Diastereoisomeric 2-octyl *p*-tolyl sulphoxides from the reaction of 2-octyl magnesium bromide with (*S*)-(−)-menthyl toluene-*p*-sulphinate have been separated[6] but not quantitatively. We have oxidized (H_2O_2, MeOH, ammonium molybdate) this same mixture of diastereoisomers and comparison of the rotation of the sulphone with a specimen claimed[6] to be optically pure, indicates that the degree of asymmetric induction is 9%.

An intriguing aspect of the behaviour of the allenic sulphoxides is that they mutarotate on standing at room temperature in acetone solution. For sulphoxide (**1**; R = *p*-tolyl) the rotation changes from $[\alpha]_D$ −120 to $[\alpha]_D$ −20° but recovered sulphoxide is unchanged in the ^1H n.m.r. spectrum. Oxidation of this recovered sulphoxide gives the sulphone with the same rotation as that obtained by oxidation of a fresh sample of sulphoxide (Scheme). This observation implies that epimerisation at sulphur occurs rapidly and without accompanying epimerisation of the allene system. Sulphoxide (**1**; R = CH_2Ph) mutarotates in acetone ($k^{40°}$ (mutarotation) = $4{\cdot}49 \times 10^{-5}\ s^{-1}$) with a rate constant comparable to that for the sulphoxide (**3**) ($k^{40°}$ mutarotation) = $1{\cdot}20 \times 10^{-4}\ s^{-1}$) for which activation parameters [$\Delta G^{\ddagger} = 24$, $\Delta H^{\ddagger} = 22$ kcal mol^{-1}, and $\Delta S = -6$ e.u.] have been determined. These values are similar to those obtained for the racemisation of allylic sulphoxides[7] in which it is clear that racemisation occurs by sulphoxide–sulphenate equilibration. If this pathway is followed, then in the reaction (1), chirality is transferred specifically between the allene system in (**1**) and the asymmetric carbon atom in (**7**), and these escape racemisation, while it occurs at sulphur. This situation has a precedent in that attempted synthesis of a chiral propargylic sulphenate ester leads[3] only to the rearranged sulphoxide with induction of asymmetry in the allene system [(**7**) → (**1**) in reaction 1]



(**1**) (**7**)

(1)

If, however, pyramidal inversion is the mechanism, the allene system must be playing a role in reducing considerable $\Delta G^{\ddagger}$ (epimerisation) at sulphur because typical values[8] for saturated sulphoxides are in the region of 40 kcal mol^{-1}. The chiral sulphoxides (**4**), (**5**) and (**6**) are, however, optically stable in the conditions which cause epimerisation of sulphoxides (**1**) and we, therefore, favour the former alternative.

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