# Asymmetric Selection *via* Elimination. A Novel Route to Partially Resolved Sulphoxides

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*Summary* Elimination reactions between β-halogenoethyl aryl sulphoxides and optically active bases provide a useful route to partially resolved sulphoxides whose configuration is dependent upon the nature of the chiral reagent and of the leaving group.

There are few examples embodying asymmetric selectivity in elimination reactions.[1,2] Most frequently, the procedure involves loss of a chiral unit with formation of an optically active olefin. In a few exceptions[3] a chiral base has been used for asymmetric destruction thus permitting recovery of optically active starting material. In the cases investi-

TABLE

Reactions between optically active bases and *p*-tolyl *β*-halogenoethyl sulphoxide

| Substrate | Base | Concentration/ (M × 10) | | Time/ h | $T$/ °C | Recovered[a] (I) or (II) | | | Product[a] (III) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Substrate | Base | | | $[\alpha]^{25}$[b] | %e.e.[c] | Config.[d] | $[\alpha]^{25}_{D}$[b] | %e.e.[e] | Config.[d] |
| (I) | (−)-Quinine | 0·4 | 0·2 | 36 | 50 | +22·7° | 10·6 | *R* | −48·3° | 10·0 | *S* |
| (I) | (−)-Quinine | 0·4 | 0·2 | 13 | 100 | +22·1 | 10·4 | *R* | −45·0 | 9·3 | *S* |
| (I) | (+)-Quinidine | 0·4 | 0·2 | 36 | 50 | −30·3 | 14·3 | *S* | +75·0 | 15·5 | *R* |
| (I) | (+)-Cinchonine | 0·4 | 0·2 | 36 | 50 | −24·8 | 11·4 | *S* | +46·8 | 9·7 | *R* |
| (I) | (−)-Cinchonidine | 0·4 | 0·2 | 36 | 50 | +16·5 | 7·5 | *R* | −42·2 | 8·7 | *S* |
| (II) | (−)-Quinine | 1·0 | 0·5 | 24 | 100 | −52·5 | 22·8 | *S* | +97·5 | 20·1 | *R* |
| (II) | (−)-Quinine | 0·5[f] | 2·0 | 6 | 100 | −53·0 | 23·8 | *S* | +102·8 | 21·8 | *R* |
| (II) | (+)-Cinchonine | 0·4[f] | 1·5 | 7 | 100 | +54·1 | 24·3 | *R* | −106·5 | 22·6 | *S* |

[a] Purity of the recovered materials >98%. [b] Optical rotations in acetone (*c* 1·2). [c] The data were evaluated from the ratio between the optical rotation measured after conversion of (I) or (II) into (III) and the corrected maximum rotation of the latter compound taken from ref. 4(b), $[\alpha]^{25} = 485°$ (*c* 1·2, acetone), assuming a linear relationship between rotation and composition (see ref. 2, p. 10); maximum deviation from repetitive experiments ±0·5% for reactions of (I) and ±1% for reactions of (II); in the latter case dehydrofluorination of the recovered sulphoxide was performed with 1,8-diazabicyclo[5,4,0]undec-7-ene. [d] Configuration of the prevailing isomer. [e] The data were evaluated from the ratio of the optical rotation of the recovered vinyl sulphoxide and the maximum rotation (see footnote c). [f] Reactions quenched at half completion.

gated the partially resolved compounds have chirality associated with carbon atoms.

We report now that when sulphoxides† of type (I) and (II) react with an insufficient amount of chiral base an enantiomeric enrichment is obtained in the vinyl sulphoxide (III) produced and at the same time the unconverted substrate is enriched in the less reactive isomer.

$$\begin{array}{l|l} & \rightarrow p\text{-MeC}_6\text{H}_4\text{SOCH}=\text{CH}_2 \\ & \quad\text{(III)} \\ 2(R,S)\text{-}p\text{-MeC}_6\text{H}_4\text{SOCH}_2\text{CH}_2\text{X}+\text{B-} & \quad(\text{excess of } R \text{ or } S) \\ \text{(I) X}=\text{Br} & \quad +\text{BH}^+ + \text{X}^- \\ \text{(II) X}=\text{F} & \\ \text{B}=\text{chiral base} & \\ & \rightarrow p\text{-MeC}_6\text{H}_4\text{SOCH}_2\text{CH}_2\text{X} \\ & \quad(\text{excess of } S \text{ or } R) \end{array}$$

Reaction of *p*-tolyl *β*-bromoethyl sulphoxide (I) with (−)-quinine, (+)-cinchonine, (+)-quinidine, and (−)-cinchonidine, in a 2:1 ratio in *NN*-dimethylformamide at 50°, after complete consumption of the base, yielded roughly the expected amount of olefin and halogeno-sulphoxide. Control experiments showed that <2—3% of the substitution product was formed, at least under the above conditions (see Table). The chirality of the predominant isomer depended on the nature of the optically active base used. The enantiomeric excess[2] is in the range 8—15%. Evaluation of these values for the olefin is straightforward since, following the Andersen method,[4a] this compound has been prepared[4b] with an optical purity of *ca.* 80%. In the case of the halogeno-sulphoxide the enantiomeric composition was evaluated after $Et_3N$-promoted transformation of (I) into (III). In a given experiment, under these conditions, the enantiomeric enrichment should be equal for product and recovered reactant. The results in the Table for each base are in fairly good agreement. The possibility of small variations in the optical composition during the work up procedure has to be taken into account, although great care was taken to prevent it and, also, the possibility of minor side reactions, *e.g.* racemization.

Higher enantiomeric enrichments (20—25%) were obtained for *p*-tolyl *β*-fluoroethyl sulphoxide (II), which behaved differently to the much faster bromo-counterpart. Indeed, in experiments performed under similar conditions the prevailing isomers have opposite configuration (see Table).

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† Satisfactory elemental analysis and n.m.r. spectra were obtained for the compounds reported.

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[4] (a) K. K. Andersen, *Tetrahedron Letters*, 1962, 93; (b) J. E. Mulvaney and R. A. Ottaviani, *J. Polymer Sci., Part A-1*, 1970, **8**, 2293.