

Optical Stability of Carbanions Derived from Sulphoximides and Sulphilimines

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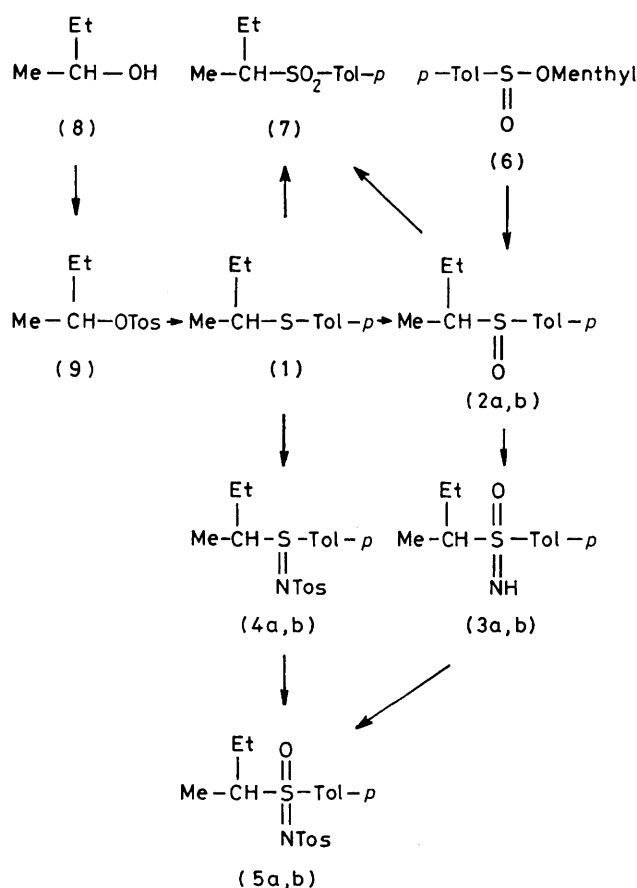
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Summary Pairs of diastereomeric sulfoximides and sulphilimines of known absolute configuration have been converted into the corresponding carbanions, which have a definite optical stability.

α -SULPHONYL- and α -SULPHINYL-CARBANIONS are widely used in organic synthesis,¹ and their configurations have been thoroughly investigated.²⁻⁴ α -Metallated sulfoximides and sulphilimines are also of great relevance, especially as nucleophilic alkylidene transfer reagents.⁵ However only a few reports have appeared on the properties of such species.^{2,4-6} A chemical study of the stability of α -sulphimidoyl carbanions has not so far been carried out, and for this purpose we prepared pairs of diastereomeric sulfoximides and sulphilimines, by the sequences reported in the Scheme.

Reaction of *p*-tolyl *s*-butyl sulphide (1) with chloramine T afforded in 90% yield a mixture of the corresponding sulphilimines (4a, b) which was oxidized by iminoperoxyacid to a mixture of the diastereomeric sulfoximides (5a, b). The sulfoximide (5b), m.p. 119–120 °C, was isolated by fractional crystallization (diethyl ether). Alternatively the sulphilimines (4a), m.p. 101 °C, and (4b), m.p. 54 °C, were isolated by fractional crystallization (diethyl ether) and column chromatography and individually oxidized to the sulfoximides (5a), m.p. 78–79 °C, and (5b).

On the assumption that oxidation by iminoperoxyacid proceeds with retention of chirality, the configuration of the sulphilimines (4a, b) is thus related to that of the sulfoximides (5a, b). Oxidation of the sulphide (1) afforded in 96% yield a mixture of the corresponding sulfoxides (2a, b), which were separated by column chromatography. Reaction of (2b) with mesitylsulphonylhydroxylamine gave the sulfoximide (3b), n_D 1.551, which was then converted into (5b) by reaction with tosyl chloride in pyridine.



SCHEME: *p*-Tol = *p*-MeC₆H₄; Tos = *p*-MeC₆H₄SO₂.

Both the Tamura-Johnson reaction⁷ and tosylation⁸ are known to be stereospecific and to proceed with retention of configuration. The sequence of reactions thus relates the configurations of (2a, b), (4a, b), and (5a, b).

Finally the absolute configurations of the sulphoxides (2a, b) and hence of (4a, b) and (5a, b) were determined by the following sequence. Reaction of (–)-menthyl (S)-toluene-*p*-sulphinate (6) with *s*-butylmagnesium bromide proceeds with inversion of chirality at sulphur to afford a mixture of (+)-(R,S)-(2b), $[\alpha]_D^{25} + 146.6^\circ$ (acetone), and (+)-(R,R)-(2a), $[\alpha]_D^{25} + 140.1^\circ$ (acetone), separated by column chromatography and individually oxidized to the corresponding sulphones (–)-(S)-(7), $[\alpha]_D^{25} - 2.2^\circ$ (acetone), and (+)-(R)-(7), $[\alpha]_D^{25} + 2.1^\circ$ (acetone). The configuration of the former was established by conversion of (–)-(R)-butan-2-ol (8), $[\alpha]_D^{206} - 15^\circ$ (neat), into the tosylate (9), $n_D^{23} 1.504$ and $[\alpha]_{589}^{13} - 6.0^\circ$ (ethyl alcohol), reaction with sodium toluene-*p*-thiolate to afford *p*-tolyl *s*-butyl sulphide (1), $n_D^{20} 1.537$ and $[\alpha]_D^{20} + 14.6^\circ$ (ethyl alcohol) and oxidation of the latter with *m*-chloroperoxybenzoic acid to *p*-tolyl *s*-butyl sulphone (7), $[\alpha]_D^{20} - 2.1^\circ$ (acetone), $n_D^{27} 1.527$. The absolute configurations are thus assigned as follows: (RR,SS)-(5a), (SR,RS)-(4a), (RS,SR)-(5b), and (RR,SS)-(4b). The optical stability of compounds (4a, b) and (5a, b) was examined by following the H–D exchange of the α -proton and the inversion reaction by ¹H n.m.r. analysis.

In pyridine as solvent in the presence of NaOD–D₂O at 20 °C, the (RR,SS)-sulphoximide (5a), m.p. 78–79 °C, and the diastereomeric (RS,SR)-(5b), m.p. 120 °C, gave complete H–D exchange in 4 and 6 h, respectively ($K_{ex} 1.4 \times 10^{-3}$ and $0.6 \times 10^{-3} \text{ mol l}^{-1} \text{ s}^{-1}$), without any appreciable inversion. Under the same conditions the sulphilimines (4a) and (4b) did not give H–D exchange in 11 days.

In the same solvent, but in the presence of CD₃ONa–CD₃OD, the sulphilimines (4b) and (4a) gave slow H/D exchange at 20 °C, the exchange amounting to 65 and 72%, respectively, after 21 days ($K_{ex} 3.3$ and $2.4 \times 10^{-6} \text{ mol l}^{-1} \text{ s}^{-1}$) and no inversion was observed. Under these conditions the sulphoximides (5a) and (5b) gave fast H–D exchange, the exchange being 70 and 66% after 6 and 8 min, respectively. Inversion also occurs, an equilibrium 1:1 mixture of (5a) and (5b) being reached after 30 min in the case of (5a) and 4 h in the case of (5b). These data show that carbanions α to sulphoximides and sulphilimines have a definite optical stability. The rates of exchange and inversion strongly depend on the solvent and base used. At least for the system studied, sulphoximides are much more acidic than sulphilimines; this is in agreement with the results of Bordwell and Johnson,^{2,5} but in contrast with a previous report.⁶

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