Optical Stability of Carbanions Derived from Sulphoximides and Sulphilimines

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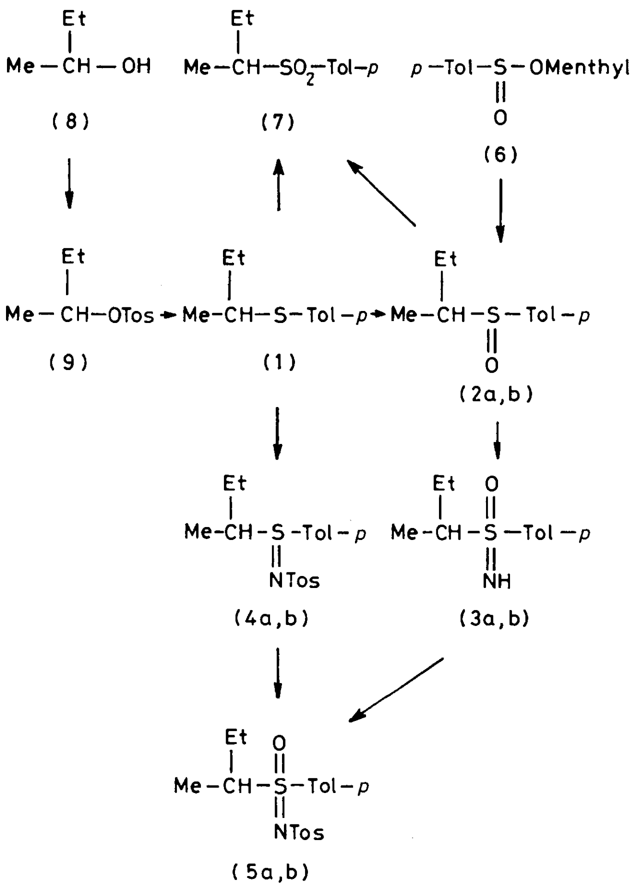
Summary Pairs of diastereomeric sulphoximides and sulphilimines of known absolute configuration have been converted into the corresponding carbanions, which have a definite optical stability.

α-Sulphonyl- and α-sulphinyl-carbanions are widely used in organic synthesis,[1] and their configurations have been thoroughly investigated.[2–4] α-Metallated sulphoximides 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 sulphoximides 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 sulphoximides (**5a**, **b**). The sulphoximide (**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 sulphoximides (**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 sulphoximides (**5a**, **b**). Oxidation of the sulphide (**1**) afforded in 96% yield a mixture of the corresponding sulphoxides (**2a**, **b**), which were separated by column chromatography. Reaction of (**2b**) with mesitylsulphonylhydroxylamine gave the sulphoximide (**3b**), n_D 1·551, which was then converted into (**5b**) by reaction with tosyl chloride in pyridine.



Scheme: *p*-Tol = *p*-MeC_6H_4; Tos = *p*-$MeC_6H_4SO_2$.

Both the Tamura–Johnson reaction[7] and tosylation[8] 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° (acetone), and (+)-(*R*,*R*)-(**2a**), $[\alpha]_D^{25}$ + 140·1° (acetone), separated by column chromatography and individually oxidized to the corresponding sulphones (−)-(*S*)-(**7**), $[\alpha]_D^{25}$ − 2·2° (acetone), and (+)-(*R*)-(**7**), $[\alpha]_D^{25}$ + 2·1° (acetone). The configuration of the former was established by conversion of (−)-(*R*)-butan-2-ol (**8**), $[\alpha]_{54}^{206}$ − 15° (neat), into the tosylate (**9**), n_D^{23} 1·504 and $[\alpha]_{589}^{13}$ − 6·0° (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° (ethyl alcohol) and oxidation of the latter with *m*-chloroperoxybenzoic acid to *p*-tolyl s-butyl sulphone (**7**), $[\alpha]_D^{20}$ − 2·1° (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 ^{1}H n.m.r. analysis.

In pyridine as solvent in the presence of NaOD–D_2O 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 × 10^{-3} and 0·6 × 10^{-3} mol l^{-1} 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 CD_3ONa–CD_3OD, 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 × 10^{-6} mol l^{-1} 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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