

EXCHANGE OF THE VINYLIC HYDROGENS OF
VINYLOGOUS SULPHINAMIDES

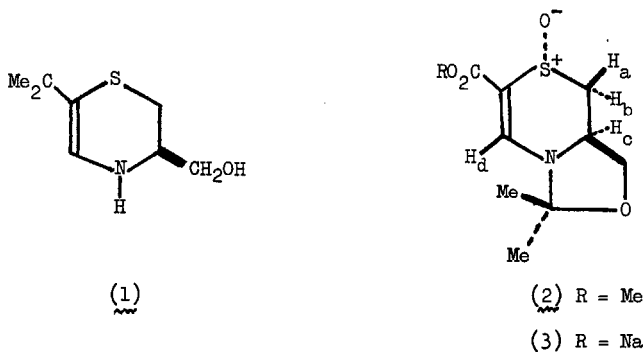
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In connection with another problem, the alcohol (1) stereoselectively monodeuterated at position 2 was required. Since the diastereotopic protons of a methylene group adjacent to a sulphoxide function can undergo base-catalysed exchange at different rates,¹ an attempt was made to replace H_a or H_b of the sulphoxide (2) by deuterium.

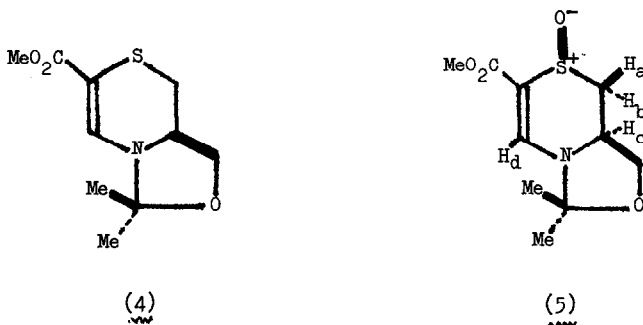
When treated with sodium deuterioxide in deuterium oxide at room temperature, the oxide (2)² was converted into the salt (3) without isotope incorporation; at 80° H_a and H_b of the salt (3) underwent deuterium exchange at a similar rate.³



In order to avoid the ester hydrolysis, the sulphoxide (2) was briefly treated with potassium *tert*-butoxide in deuterodimethyl sulphoxide at room temperature. The recovered sulphoxide⁴ was 5% tetra-, 87% tri-, and 7% mono-deuterated on the basis of mass spectroscopy; n.m.r. spectroscopy clearly revealed that H_a, H_b, and H_d had been replaced by deuterium.⁵ A control experiment established that the sulphide (4)⁶ did not incorporate deuterium under

the reaction conditions. Consequently, the exchange of the vinylic hydrogen is associated with the presence of the sulphinyl group.

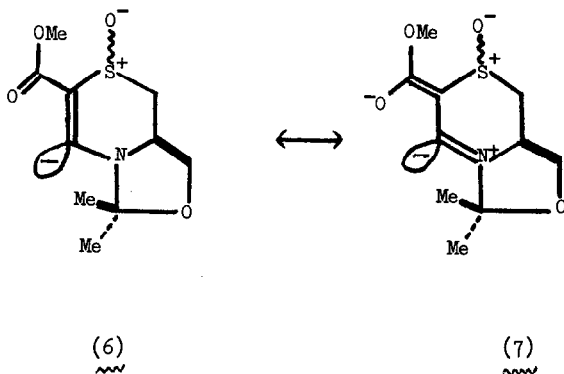
The reaction of the sulphoxide (2) with potassium tert-butoxide in deuterodimethyl sulphoxide was monitored by n.m.r. spectroscopy and quenched when the vinylic hydrogen had undergone partial exchange. The recovered sulphoxide was 16% tri-, 39% di-, 34% mono-, and 10% un-deuterated by mass spectroscopy; n.m.r. spectroscopic analysis (90 MHz) indicated that H_a had undergone 16%, H_b 54%, and H_d 69% deuterium exchange.



In order to determine if the vinylic-hydrogen exchange was sensitive to the stereochemistry of the sulphinyl group, the diastereoisomeric sulphoxide (5)² was briefly treated with potassium tert-butoxide in deuterodimethyl sulphoxide at room temperature. The recovered sulphoxide⁴ was 50% mono- and 50% un-deuterated by mass spectroscopy; only H_d had undergone isotopic exchange by n.m.r. spectroscopy (90 MHz).⁷

A competitive experiment in which a 1:1 mixture of the sulphoxides (2) and (5) was treated with potassium tert-butoxide in deuterodimethyl sulphoxide, showed that the vinylic hydrogens of the sulphoxides exchanged at a very similar rate. Consequently, the acidity of H_d is not influenced by the sulphoxide stereochemistry.

It is clear from the foregoing results that H_d of the sulphoxides (2) and (5) exchange faster than H_a and H_b . The unusual ease with which the vinylic exchange occurs suggests that the ylid (7)⁸ contributes to the stabilisation of the intermediate vinyl anion (6). A similar process had been invoked to account for the exchange of the 2- and 6-hydrogens of N-methyl-4-pyridone,⁹ which takes place in 0.5*N*-sodium deuterioxide solution at 100°.



Acknowledgements We thank Mr. P. Kelly for determining the mass spectra, Dr. N.M.S. Hill for measuring the 90 MHz n.m.r. spectra, and the S.R.C. for a research studentship (to J.K.).

References and footnotes

1. R.R. Fraser, F.J. Schuber, and Y.Y. Wigfield, J. Amer. Chem. Soc., 94, 8795 (1972) and references therein.
2. J. Kitchin and R.J. Stoodley, Tetrahedron, accepted for publication.
3. The n.m.r. spectrum (60 MHz, D₂O) of the salt (3) showed signals at τ 7.65 (1H, t, J_{ab} , J_{ac} 13.2 Hz) for H_a, 6.51 (1H, dd, J_{ab} 13.2, J_{bc} 2.6 Hz) for H_b, and 1.96 (1H, s) for H_d.
4. This material was identical to the starting sulphoxide on the basis of its m.p., optical rotation, and chromatographic mobility.
5. The n.m.r. spectrum (90 MHz, CDCl₃) of the sulphoxide (2) showed signals at τ 7.98 (1H, t, J_{ab} , J_{ac} 12.8 Hz) for H_a, 6.82 (1H, dd, J_{ab} 12.8, J_{bc} 2.6 Hz) for H_b, and 2.15 (1H, s) for H_d.
6. A.R. Dunn and R.J. Stoodley, Tetrahedron, 28, 3315 (1972).
7. The n.m.r. spectrum (220 MHz, CDCl₃) of the sulphoxide (5) showed signals at τ 7.34 (1H, t, J_{ab} , J_{ac} 12.0 Hz) for H_a, 6.27 (1H, dd, J_{ab} 12.0, J_{bc} 2.5 Hz) for H_b, and 2.38 (1H, s) for H_d.

8. This formulation is not intended to exclude the possibility that the π -electrons are also delocalised in the sulphur d-orbitals; however, calculations [A. Rauk, S. Wolfe, and I.G. Csizmadia, Canad.J.Chem., 47, 113 (1969)] suggests that this effect is likely to be unimportant. The salt (3) does not undergo vinylic-hydrogen exchange in the presence of potassium tert-butoxide and deuterodimethyl sulphoxide and, consequently, the methoxy-carbonyl group of the sulphoxide (2) is necessary for the exchange reaction.
9. P. Beak and J. Bonham, J.Amer.Chem.Soc., 87, 3365 (1965).