Stereoselective Deuterium Exchange of Methylene Hydrogens of Benzyl *p*-Chlorophenyl Sulphoxide

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A DIFFERENCE in the rates of exchange of the two methylene hydrogens of benzyl methyl sulphoxide[1] and phenylsulphoxyacetic acid[2] has been reported. It was not clear, however, which of the hydrogens is preferentially exchanged, and neither was the mechanism whereby the hydrogen exchange is stereospecific.

In previous papers,[3,4] we have shown that it is possible to make an absolute assignment of individual methylene protons of benzyl *p*-substituted phenyl sulphoxides (p-$R^1{\cdot}C_6H_4{\cdot}SO{\cdot}CH_2{\cdot}C_6H_4R^2$) by an examination of substituent and solvent effects on the proton resonances of these compounds. It was shown that the equatorial proton (H_{eq}) of 3-benzylidene thiochromanone 1-oxide (I)† shows a larger solvent shift in trifluoroacetic acid (TFA) relative to deuteriochloroform ($\Delta - 0{\cdot}50$ p.p.m.) than does the axial proton (H_{ax})‡ ($\Delta - 0{\cdot}31$ p.p.m.). This evidence led us to the conclusion that the upper part of the methylene AB-quartet of benzyl *p*-chlorophenyl sulphoxide (II) {in $CDCl_3$, τ $[(A + B)/2]$ 5·98, J_{AB} 12·5 c./sec., τ_{AB} 0·09} corresponds to the proton *trans* (H_A) and the lower part to the

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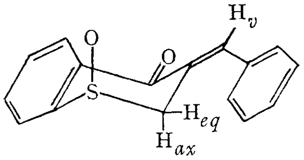
† The S–O group is considered to have the axial configuration because of the large difference in Δ for H_{ax} and H_{eq}, since such a discrepancy cannot be explained if S–O has the equatorial configuration.

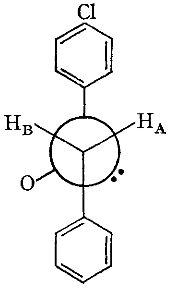
‡ Assignment of these protons was made by an observation of allylic long-range coupling (J_{ax-v} 1·5 c./sec.) for H_{ax}.

proton *gauche* (H_B)§ with respect to the S–O bond.¶ In contrast, for an acetone solution of



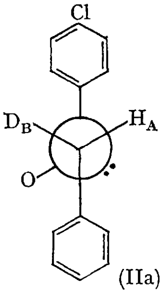
(I)

the same compound, it is the lower part of the AB-quartet {τ [(A + B)/2] 5·90, J_{AB} 12·5 c./sec., τ_{AB} — 0·11} which is assigned to the proton *trans* (H_A) with respect to the S–O bond.

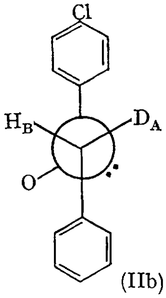


(II)

Examination of the n.m.r. spectra of the partially exchanged compound revealed the same phenomenon as observed by Bullock and his co-workers: as AB-quartet of the non-exchanged sulphoxide (I) is superimposed on two broad peaks of unequal intensity (see Figure) appropriate to the diastereoisomers (IIa) and (IIb). The unequal intensity of the peaks corresponding to the diastereomeric sulphoxides (IIa) and (IIb) must be a consequence of differing exchange rates for H_A and H_B in (II). From an examination of the relative intensities of these signals, it is concluded that H_B (*gauche* to the S–O bond and *trans* to the



(IIa)



(IIb)

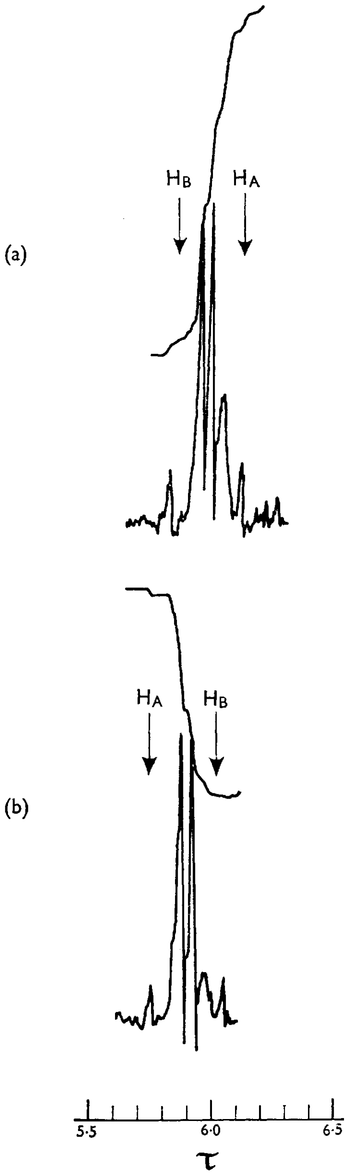


FIGURE. *N.m.r. spectra of partially exchanged benzyl* p-*chlorophenyl sulphoxide* (0·03 M NaOD–D_2O–*dioxan,* 55°, 10 *min., quenched with ice–dilute* HCl *and recrystallized*) *in deuteriochloroform* (a) *and acetone* (b)

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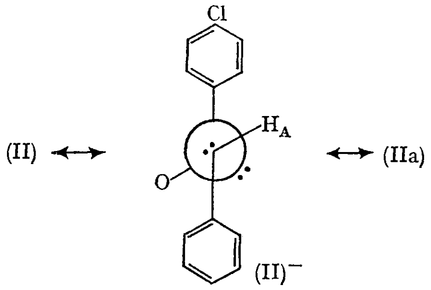
§ This proton is more sensitive to the addition of TFA (ref. 4).

¶ It has been established that the donor resides on the oxygen atom of the S–O group in a sulphoxide–TFA complex (ref. 4).

lone pair on sulphur) is exchanged more rapidly than H_A.

At least two possibilities should be considered in assigning stereochemistry to the asymmetric α-sulphinyl carbanion: (1) the anion is asymmetric because the charge-bearing α-carbon has a pyramidal structure with a barrier to configurational inversion; (2) the structure of the carbanion is planar, but the possibilities of deuterium cation approach from the two sides are not equal.



(II)$^-$

While open to further suggestions, we believe that the mechanism (1) is more likely, and that the reaction proceeds with retention of configuration, since the incipient carbanion (II)$^-$ can be stabilized by charge-transfer hyperconjugation with the unshared electron pair on the sulphur atom.

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[1] A. Rauk, E. Buncel, R. Y. Moir, and S. Wolfe, *J. Amer. Chem. Soc.*, 1965, **87**, 5498.

[2] E. Bullock, J. M. W. Scott, and P. D. Golding, *Chem. Comm.*, 1967, 168.

[3] M. Nishio, *Chem. and Pharm. Bull.* (*Japan*), 1967, **15**, 1669.

[4] M. Nishio, *Chem. and Pharm. Bull* (*Japan*), submitted for publication.