On the Conformational Preference of an α-Sulphonyl Carbanion

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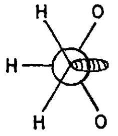
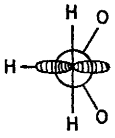
Summary In the base-catalysed hydrogen-deuterium exchange of a conformationally-fixed sulphone, (IV), the relative rates of exchange of the diastereotopic protons α to the sulphone group indicate the stability of the resultant carbanions to be qualitatively in agreement with M.O. theory but less sensitive to orientation than was predicted.

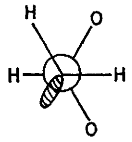
THE acid-strengthening effect of a sulphonyl group on an adjacent C–H proton is a well documented fact attributed to *d*-orbital stabilization of the resultant carbanion.[1] The stereochemical behaviour of this carbanion, when formed from an asymmetric carbon atom, has been studied.[1-3] Both tetrahedral[2] and trigonal[2,3] carbanions have been proposed as intermediates. Most recently, non-empirical molecular orbital calculations have predicted[4] the most stable conformation of the anion $-CH_2SO_2H$ to be (I). The planar carbanion (II) was calculated to be 2·5 kcal less stable than (I). A 120° rotation about the C–S bond of (I) gives (III), which was calculated to be 4·1 kcal. less stable than (I). We report the first study of the exchange rates of two diastereotopic protons α to a sulphonyl group specifically in sulphone (IV)† in order to test these predictions.



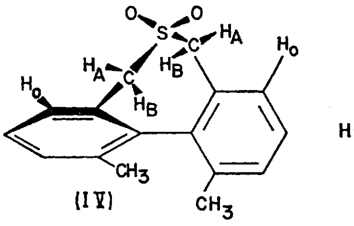
(I)



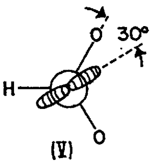
(II)



(III)



(IV)



(V)

The sulphone (IV) was heated at 80° in t-butyl alcohol–0·03M-sodium phenoxide. Exchanges were conducted for 20, 60, and 120 min. and each quenched product was examined by n.m.r. In comparison with the n.m.r. of (IV), which contained an AB quartet [δ_A 4·220, δ_B 3·732 and J_{AB} = 13·7 Hz in $(CD_3)_2SO$] for the four benzylic protons, the exchanged sulphone samples showed unequally diminished signals for the remaining A and B protons. By careful integration‡ of the benzylic region, relative to the methyl group absorption, a quantitative determination of the proportions of H_AH_B [unexchanged (IV)] D_AH_B, H_AD_B and D_AD_B components was possible. Since the mathematical expressions for the kinetics of two competitive consecutive reactions were too complex for immediate solution, the data for each exchange was analysed by the "best fit" method using the scheme

$$\begin{tikzcd}
H_AH_B \arrow[r, "k_A"] \arrow[dr, "k_B"'] & D_AH_B \arrow[r, "k'_B"] & D_AD_B \\
 & H_AD_B \arrow[ur, "k'_A"'] &
\end{tikzcd}$$

$k_A + k_B$ was determined from the disappearance of H_AH_B, a value of the isotope effect k_A/k'_A was assumed; k_A/k_B could then be determined from the concentration of D_AH_B and checked against the concentration of H_AD_B.

Good agreement for each set of data was found for an isotope effect of 1·2 and $k_A/k_B = 3$ (±0·5 estimated error).§ The value for the secondary isotope falls within the expected range, being similar to the value, 1·15, reported[5] for the exchange of the methyl protons of toluene.

Since a Dreiding model of (IV) revealed a significant difference in the accessibility of its diastereotopic protons, a second set of exchanges was performed with a hindered base, namely 2,6-dimethylphenoxide. In this case k_A/k_B was found to be 7·5 ± 0·5. It can thus be concluded that, in the absence of steric effects, k_A/k_B would be less than 3.

The assignment of peaks for the A and B protons of (IV) was accomplished by use of the Nuclear Overhauser Effect.[6] Experiments[7] on degassed solutions of (IV) in $(CD_3)_2SO$ and on two samples deuteriated selectively at H_A and at H_B showed that H_A (22% NOE) lies closer to the *o*-aromatic protons than H_B (0% NOE). Thus H_A represents the Pro-*S* proton in (*R*-IV) and the Pro-*R* proton in (*S*-IV). From an examination of a Dreiding model of (IV) the C–H_A bond is seen to be oriented 10° from the bisector of the O–S–O projected angle, the C–H_B bond 110° from this bisector. Since the relative rate of exchange, $k_A/k_B = 3$, the difference in transition states leading to carbanions (I) and (III) amounts to 0·76 kcal. If a Brønsted correlation between kinetic and thermodynamic acidities is valid in our case, with a slope[8] of 0·7, then the difference in the free energies of carbanions (I) and (III)¶ should not exceed 1·1 kcal. This value is significantly smaller than that calculated for $\cdot CH_2\cdot SO_2H$.[4] The energy difference will also depend on the activating influence of the adjacent phenyl ring. This effect which preferentially stabilizes the carbanion derived from H_B-abstraction is probably offset by the steric effect favouring H_A-abstraction. We can tentatively estimate the effect to be 0·4 kcal. as follows.

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† A satisfactory C and H analysis of (IV), which was prepared from the known sulphoxide (R. R. Fraser and F. J. Schuber, *Chem. Comm.*, 1969, 397) was obtained.

‡ All spectra and their integrations were performed on a Varian HA-100 spectrometer in the field sweep mode during simultaneous deuterium spin-decoupling using an N.M.R. Specialties SD-100 decoupler.

§ That the small stereoselectivity was not due to racemization during the exchange was proved by the observation that the proportions of diastereomeric monodeuteriosulphones remained unchanged after heating for 150 min. at 85°.

¶ To equate the carbanions derived from (IV) to (I) and (III), in spite of a 10° difference in their geometries, involves only a 0·3 kcal. difference in their calculated (ref. 4) stabilities.

If the observed ten-fold enhancement of exchange by phenyl over hydrogen for an α-sulphonyl carbanion[3a,9] is half due to resonance stabilization,[9] a freely rotating phenyl group provides 0·68 kcal. stabilization. Since H_A and H_B are oriented 70 and 50° from colinearity with the adjacent π-electrons, a $\cos^2\phi$ relation predicts the difference in their stabilizations to be $(2 \times 0{\cdot}68)$ $(\cos^2 70° - \cos^2 50°)$ = 0·40 kcal.

A second possibility for the exchange of (IV) is that the sp^2 carbanion shown in (V) is formed by abstraction of either proton. The nearness of the p-orbital to the adjacent S–O bond has been cited as an unstable conformation on electrostatic grounds[2e] but its possible participation cannot be eliminated by the available evidence. Nevertheless, either explanation of our results indicates that the predictions of M.O. theory are qualitatively correct, but appear to overestimate the energy differences.

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