THE   DYNAMIC   STEREOCHEMISTRY   OF   HALOGENOSULPHENAMIDES

AND   HALOGENOSULPHONAMIDES

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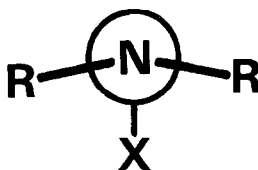Department of Chemistry, Queen's University, Belfast BT9 5AG

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N.m.r. measurements at 35°C on individual solutions of chloro- and bromo-N,N-diethylsulphenamide, Et_2NSX in toluene-d_8 (0.68 M) showed sharp triplets and quartets for the ethyl signals.   Mixed solutions of similar concentration in this solvent showed sharp signals at τ values intermediate between those of the pure compounds at temperatures above +50°C.   Below -40°C distinct signals were observed attributable to each of the separate components.   Halogen exchange is rapid for solutions of this concentration above 50°C.   Mixtures in dichloromethane (0.58 or 1.15 M) showed evidence for much faster halogen exchange in that individual spectra were only achieved at temperatures ca. -80°C.   These results have important implications in the interpretation of the variable temperature n.m.r. spectra of the halogeno-sulphenamides.

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Previous work[1] has shown that nitrogen inversion is rapid for acyclic sulphenamido compounds, and that the ground-state conformation around the NS bond is as shown in 1.   Therefore both N-S torsion and sulphur inversion must become slow on the n.m.r. time-scale for geminal non-equivalence to be observed in compounds possessing prochiral N-alkyl substituents (eg. R = Pr[i]). Although configurational stability at sulphur is usually high[2], it has been recognised recently that halogen exchange in halogenosulphinamides $(R_2NS(O)X)$ can occur readily in solution at ambient temperature with inversion at sulphur.[3] Thus the rate process measured in halogenosulphenamides (1) by the dynamic n.m.r. technique could refer to either torsion or halogen exchange.

The geminal methyl groups and methylene protons of diisopropyl- and diethyl-aminosulphenyl chloride respectively $(1, R = Pr^i$ and Et; X = C$\ell)$ in toluene-d_8 solution became diastereotopic on the n.m.r. time-scale in the temperature range 0 to 30°C.   In the diisopropyl compound $\Delta G^{\ddagger}$ was determined[4] to be 60·8 kJ mol^{-1} at the coalescence temperature (5°); moreover the coalescence temperature was similar for 0·09 and 0·48 M solutions.   On the basis that halogen exchange is a bimolecular process[3,5], the concentration independence suggests that sulphur inversion is not the observed rate process. Raban and Cho[6] have recently interpreted the variable temperature spectrum of chloro-N,N-benzyl,isopropylsulphenamide in toluene-d_8 in terms of torsion around the NS bond.   We have found that the coalescence temperature of the methylene protons remained essentially constant at 28±2° for 0·17, 0·45, and 0·93 M solutions in toluene-d_8, thus the reported free energy of activation does indeed appear to refer to bond rotation.   However, in dichloromethane solution these three sulphenamides did not show any signal splitting down to -60°.   It seems unlikely that this could be due to accidental equivalence in all cases, and it is possible that chlorine exchange is more rapid in this solvent.   This would be in accord with the observations on the mixed chloro- and bromo- compounds discussed above.

The conditions whereby prochiral substituents in a chlorosulphonamide e.g. chloro-N,N-dibenzylsulphonamide, $Bz_2NSO_2C\ell$ (2) become diastereotopic are similar to those for sulphenamides.   It was thus necessary to confirm that

the published barriers to dynamic exchange in chloro-sulphonamides[7] were due to restricted rotation around the NS bond and not to halogen exchange.   Spectra of (2), measured for solutions 0·10, 0·33, and 0·66 M in deuteriochloroform, gave all cases T_C -58 ± 2°C with $\Delta\nu_{AB}$ 10·3 Hz at 60 MHz, J_{AB} 15·0 Hz, and $\Delta G^{\ddagger}$ 46·2 kJ mol^{-1},[8] similar to the value quoted in CHCℓ_2F solution.[7]   Solutions of (2) 0·057 and 0·49 M in toluene-d_8 again gave a constant value of T_C -50 ± 2°C with $\Delta\nu_{AB}$ 25·0 Hz at 60 MHz, J_{AB} 14·9 Hz, and $\Delta G^{\ddagger}$ 45·6 kJ mol^{-1}.   Thus the measured values do refer to torsion around the NS bond.

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4.   Calculated from $k_c = \pi \, \Delta\nu / 2^{\frac{1}{2}}$ and the Eyring equation ($\Delta\nu$ 9.6 Hz at
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8.   Calculated from $k_c = \pi \, (\Delta\nu^2 + 6J^2)^{\frac{1}{2}} / 2^{\frac{1}{2}}$ and the Eyring equation.