Sulphenimines: A New Synthesis and Barriers of Stereomutation

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Summary Sulphenimines (**1a**—**e**) were prepared from aryl disulphides, silver nitrate, ammonia, and acetone and their barriers of stereomutation were shown to be insensitive to substituent effects.

INTEREST in the type of bonding between sulphur and nitrogen in sulphenamides,[1] electronegativity effects on the barriers to pyramidal inversion in phosphines,[2] and stereomutation in imines[3] prompts us to report a new synthesis of sulphenimines (**1a**—**e**) and their barriers of stereomutation.

Acetone arylsulphenimines (**1a**—**e**) (**a**; X = H, **b**; X = 4-Cl, **c**; X = 4-Br, **d**; X = 3-NO$_2$, **e**; X = 4-NO$_2$) were prepared (reaction 1) from one equivalent each of silver nitrate and aryl disulphide, excess of acetone, and ammonia in methanol. Their properties are summarized in the Table.

The n.m.r. spectra of the diastereotopic methyl groups in (**1a**—**e**) consisted of a doublet at ambient temperature which reversibly coalesced to a singlet at 105—116°. Using

$$(XC_6H_4S)_2 + AgNO_3 \xrightarrow[NH_3]{Me_3CO} \underset{(\mathbf{1a}\text{—}\mathbf{e})}{XC_6H_4SN{=}CMe_2} + AgSC_6H_4X \qquad (1)$$

the equation $k_C = \Delta\nu_0\pi/\sqrt{2}$ for the rate of exchange at coalescence and the Eyring equation, the free energies of activation ($\Delta G^\ddagger$) for stereomutation in (**1a**—**e**) were calculated (Table).

It was necessary to estimate a value for $\Delta\nu_0$ since a plot of $\Delta\nu$ *vs.* temperature after coalescence increased linearly as the temperature decreased.† This phenomenon is well known[4] and suggests changes in conformer populations.

Despite the necessity of estimating $\Delta\nu_0$, the barriers in (**1a**—**e**) of 20 kcal are in reasonably close agreement with the values of 23 kcal predicted for $CH_2=N-S$ based on electronegativities.‡ Furthermore, an increase of $\Delta\nu$ by 50% only increases $\Delta G^\ddagger$ by 0·3 kcal (see Table).

Steric and electronic effects have been used to explain the differences of 5—40 kcal for the barriers of stereomutation in *N*-substituted imines.[5] The positive value for the Hammett reaction constant in *p*-substituted aryl imines has been explained in terms of (*p*–*p*) π conjugation which stabilizes the linear transition state.[5b,6] More recently the barrier in *N*-germyl imine has been interpreted in terms of electronegativity effects.[3]

Properties of acetone arylsulphenimines (**1a**—**e**)

Compound[a]	M.p. (b.p.)	Yield (%)	$\Delta\nu_{-40}$ (Hz)	$\Delta\nu_{40}$ (Hz)	T_c (°C)	K_c (−40) (s^{-1})	K_c (40) (s^{-1})	$\Delta G^\ddagger$ (−40) (kcal)	$\Delta G^\ddagger$ (40) (kcal)
(**1a**)	66 (0·5 mm)	60	9·4	6·0	104·5	20·9	13·3	20·0	20·3
(**1b**)	39—40	60	9·4	6·3	110·0	20·9	14·0	20·3	20·6
(**1c**)	48—49	65	9·0	6·4	111·5	20·0	14·2	20·4	20·7
(**1d**)	50—51	80	7·5	6·6	108·0	16·7	14·7	20·4	20·5
(**1e**)	93—94	94	9·3[b]	7·3	116·0	20·7	16·2	20·6	20·8

[a] All compounds and elemental analysis, i.r., and n.m.r. spectra consistent with their structures. [b] Extrapolated. (**1e**) precipitated from solution at −20°.

There is compelling evidence for donation of electrons from nitrogen to sulphur in the ground state of arylsulphenanilides. This effect has been estimated to contribute a minimum of 7 kcal to the S–N torsional barrier[1a] and to explain the differences in rates of nearly 10^3 for bimolecular displacement reactions at the S–N bond.[1b] In order to explain the dependence of (*p*–*d*) π bonding on the dihedral angle Raban has argued that one sulphur *d*-orbital overlaps with both the aromatic π system and the nitrogen lone pair in the ground state but not the transition state.[1a]

Donation of the nitrogen lone pair to sulphur should be even better in sulphenimines than in sulphenamides since calculations suggest that delocalization of a lone pair of electrons into an adjacent atom containing *d*-orbitals will be at a maximum when the lone pair is in a *p*-orbital.[7] It is surprising, therefore, that the barriers in (**1a**—**e**) are relatively insensitive to a change in the substituent X. Brown and his co-workers have reported somewhat similar results for the barriers in 4,4′-dimethylbenzophenone 4-chloro- and 2,4-dinitrobenzenesulphenimine (18·5 and 18·6 kcal mol^{-1}).[8]

There are at least two possible explanations for these results. First, the barriers in (**1a**—**e**) will be insensitive to a change in the substituent if there is no interaction between sulphur and the nitrogen lone pair and the change in the electronegativity of the sulphur is small. Rotation about the S–N bond, which may be important in (**1a**—**e**) even at low temperatures, would destroy the (*p*–*d*) π bond if it is dependent on the dihedral angle.[1a]

Alternatively, the barriers in (**1a**—**e**) will be insensitive to a change in the substituent if donation of electrons from nitrogen to sulphur stabilizes both the ground and transition states for stereomutation.

The u.v. spectra of (**1a**—**e**), at least in part, support the latter interpretation and suggest that there is delocalization of the nitrogen lone pair into the aromatic π system. The u.v. spectra of (**1a**—**c**) (cyclohexane) had λ_{max} at 272—280 nm (ϵ 11,200—20,000) whereas (**1d**) and (**1e**) had λ_{max} at 345 (ϵ 1160) and 340 (ϵ 18,400), respectively. In ethanol a bathochromic shift (5 and 11 nm) was observed for (**1d**) and (**1e**). This anomalous solvent shift has been attributed to removing the nitrogen lone pair from conjugation with the *N*-phenyl group in *N*-benzylideneaniline.[9]

Two mechanisms have been considered for stereomutation in sulphenimines; planar nitrogen inversion and torsion about the C–N double bond.[5] The similarity in structural effects on the barriers in imines and aziridines has been used as evidence for the inversion mechanism in imines. The barriers of pyramidal inversion in sulphenylaziridines show the same insensitivity to substituent effects as do (**1a**—**e**).[10]

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† A value for $\Delta\nu_0$ was assigned at −40° ($\Delta\nu_{-40}$) from the plots of $\Delta\nu$ *vs.* temperature for (**1a**—**e**). This effect was observed in different solvents and persisted at the lowest temperature obtainable.

‡ This value was estimated from a plot of Allred electronegativities of X *vs.* the calculated barriers of planar nitrogen inversion in $CH_2 = N-X$ reported by Cook and Mislow; see ref. 3.

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