An Ambident Carbanion Stabilized by Bivalent Sulphur

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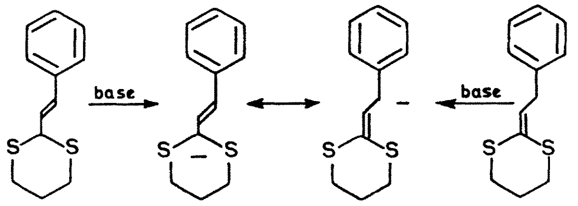
Summary 2-α-Styryl-1,3-dithian reacts with strong bases to yield an ambident carbanion: the importance of sulphur 3*d*-orbital conjugation in the stabilization of such ambident carbanions is assessed with CNDO calculations.

THE enhanced acidity of hydrogen atoms on carbon atoms adjacent to bivalent sulphur atoms was first observed thirty years ago.[1] Although the chemistry of the conjugate bases has been developed extensively, particularly in recent years,[2] no one mechanism for the stabilizing effect of sulphur has gained universal acceptance.[3] Largely by analogy with the *d*-orbital model for sulphone-stabilized carbanions,[4] *d*-orbital conjugation has been advanced to explain the stabilization of carbanions by bivalent sulphur.[5-7]

In a recent paper[8] Wolfe and his co-workers have used the results of *ab initio* MO calculations in support of the view that *d*-orbital conjugation is not a significant factor in the stabilization of carbanions by adjacent sulphone groups. Application of this method to a carbanion stabilized by bivalent sulphur enabled them to compute a preferred conformation for such anions. Since inclusion of *d*-orbitals in the GTO basis set did not improve the results, it was inferred that the stabilization of such carbanions "can be interpreted without resort to a postulate of *d*-orbital conjugation."[9] The question of *d*-orbital involvement in the chemistry of bivalent sulphur compounds remains a contentious one, particularly in the case of thiophen[10] where it was first advanced on experimental grounds[11] and has since been both endorsed and disputed on theoretical grounds.

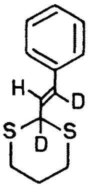
While the principal value of this model is that it brings several features of the chemistry of bivalent sulphur compounds into a coherent descriptive framework,[12] it is also of some predictive value. For example, it assigns an essentially π-character to the carbanion stabilization effect and therefore predicts that it will be transmissible through a π-electronic system. We describe an experimental verification of this prediction.

2-α-Styryl-1,3-dithian (**1**), readily prepared from cinnamaldehyde and propane-1,3-dithiol, was selected for detailed study. The conjugate base of this dithian can be easily generated and has been shown by three types of experiments to be the ambident anion represented by resonance structures (**2**) and (**3**).[13]



(1) (2) (3) (4)

Isomerization experiment. When a sample of the dithian (**1**) is heated with $KOBu^t$ in Bu^tOH at 110°, it is partly isomerized to a mixture of (**1**) and the keten-thioacetal (**4**). Compound (**4**) is readily isolated either by preparative layer or column chromatography and its structure established by i.r., n.m.r., and m.s. techniques. An equilibrium mixture of compounds (**1**) and (**4**) (*ca.* 1 : 2) can be obtained by exposing either to these reaction conditions. *Deuterium-exchange experiment.* When a sample of the dithian (**1**) is heated with $KOBu^t$ in Bu^tOD at 110° (42 h), it is changed to a mixture of the doubly deuteriated compounds (**5**) and (**6**) (n.m.r. and m.s. analysis of separated compounds). *Alkylation experiment.* A sample of the dithian (**1**) was converted into its conjugate base by treatment with n-butyl-lithium.† Quenching the anion with an excess of methyl iodide gave a mixture of the methylated derivatives (**7**) and (**8**) (*ca.* 1 : 1). The vinylic protons of (**7**) appear as doublets at 6·15 and 6·80 p.p.m. (*J* 16 Hz) and the vinylic and benzylic protons of (**8**) appear as a doublet at 5·99 (*J* 10 Hz) and a multiplet at 3·81 p.p.m. respectively.



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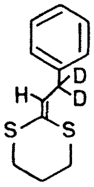

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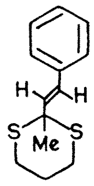

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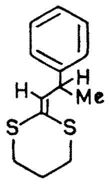

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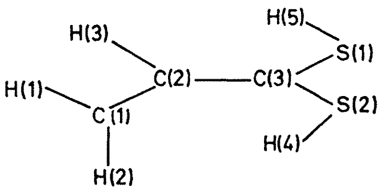
These experiments establish (i) that the conjugate base of dithian (**1**) is the ambident anion (**2**) ⟷ (**3**), and (ii) that the acidifying effect of bivalent sulphur is transmitted through the double bond of compound (**4**) to its benzylic hydrogen atoms.



(9)

In order to assess the role of sulphur *d*-orbitals in the stabilization of this carbanion, semi-empirical CNDO MO calculations[14] were carried out on the (planar) model system (**9**) both with and without *d*-orbitals in the basis set. The results of these calculations are given in the Table in terms of the excess of charge and π-electron distribution. The contributions of the sulphur atoms to the anion stabilization is greater with the *d*-orbitals included but the enhancement is small. The π-electron densities on sulphur are increased by only 10% and the negative charges on sulphur

† Experiments designed to assess the importance of carbon–lithium covalent bonding in lithiated thioacetals are in progress.

Atom		H(1)	H(2)	H(3)	H(4)	H(5)	C(1)	C(2)	C(3)	S(1)	S(2)
Excess charge[a]	..	−0·04	−0·01	−0·05	+0·02	−0·11	−0·28	+0·15	−0·17	−0·23	−0·26
Excess charge[b]	..	−0·07	−0·05	−0·08	+0·07	−0·04	−0·38	+0·09	−0·19	−0·16	−0·21
π-Electron density[a]	..						1·36	0·89	1·39	2·18	2·18
π-Electron density[b]	..						1·53	0·92	1·58	1·99	1·99

[a] *d*-Orbitals included. [b] *d*-Orbitals not included.

by about 25%. The calculation suggests that the contribution of *d*-orbital resonance could be significant but may not be essential to the carbanion stabilization.

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