Tetrahedron Letters,Vol.25,No.13,pp 1411-1414,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

HAMMETT INVESTIGATION OF IODIDE-ION-INDUCED DEOXYGENATIVE REDUCTION OF 2-ARYL'SULPHONYL-3-ARYLOXAZIRIDINES IN METHANOL-WATER (50% v/v).

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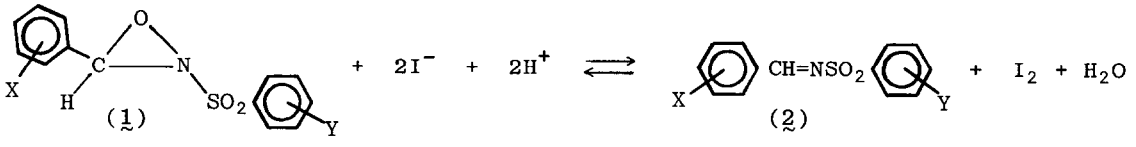
The Hammett substituent dependence of the iodide ion induced deoxygenation of 2-aryl'sulphonyl-3-aryloxaziridines, in aqu. methanol suggests that the reaction proceeds by nucleophilic attack on oxygen with concomitant O-N bond breakage.

Oxaziridines were first characterised[1-3] in 1956-57 and can be routinely prepared by low-temperature peracid oxidation of the corresponding imines[4]. Oxaziridines have attracted the attention of synthetic chemists because they are strong, yet selective, oxidants which can be used for oxidation of sulphides to sulphoxides, or disulphides to thiosulphates etc.[5] This prompted Davis and co-workers[6] to synthesise a series of 2-aryl'sulphonyl-3-aryloxazirines (1) (by oxidation of the corresponding sulphonimine with m-chloroperbenzoic acid), which are the first examples of oxaziridines to have substituents other than carbon attached to the ring nitrogen and are characterised by a highly electrophilic ring oxygen. These compounds, which have been shown to be of E-configuration[6,7,8] can be prepared in optically active form and have potential for asymmetric oxidation of a wide range of substrates.

As an extension of our studies of ring-opening reactions of 3-membered heterocycles (which recently included a Hammett study of 1-aryl'sulphonyl-2--arylaziridines) we have been prompted to conduct a limited study of the directly analogous 2-aryl'sulphonyl-3-aryloxaziridines (1) reported by Davis et al. In this communication we report the results of a Hammett study of the iodide-ion induced deoxygenation of (1) in 50% v/v methanol-water at 25°.



(1) (2)

The substrates (1), which were prepared from the corresponding imines (2) as described previously[6], were characterised by pmr, cmr and elemental analysis and had the following melting points (X, Y, m.p.: p-MeO, p-Me, 98°; p-Me, p-Me, 88; H, p-Me, 114; p-Cl, p-Me, 87; p-Br, p-Me, 82; m-Cl, p-Me, 147; p-NO_2, p-Me, 98; H, p-MeO, 98; H, H, 97; H, p-Br, 88; H, m-NO_2, 97. Reactions of (1) (1×10^{-4}M) with 0.002-0.1M KI were monitored at 350 nm (absorption maximum for I_3^-) using a Canterbury stopped-flow system. Pseudo-first order rate data was processed by least squares analysis in the usual way. A rectilinear relationship between k_{obs} and $[I^-]$ was obtained, in each case, from which the second order rate constant could be determined (Table 1); iodide-independent reactions did not compete under the conditions described.

Table 1

Second order rate constants for reaction of oxaziridines (1) with potassium iodide (0.002-0.1M) in 50% v/v methanol-water at 25°

X	Y	$k/M^{-1}s^{-1}$	X	Y	$k/M^{-1}s^{-1}$
p-Me	p-Me	77	H	p-OMe	77
H	p-Me	102	H	p-Me	102
p-Cl	p-Me	187	H	H	162
p-Br	p-Me	180	H	p-Br	210
m-Cl	p-Me	228	H	m-NO_2	505
p-NO_2	p-Me	663			

The stoichiometry of reaction between oxaziridines and potassium iodide is well established and has previously been used to advantage in iodometric assay of oxaziridine purity.[1,6] However, the mechanism of this deoxygenative imine forming reaction has not been probed for reaction of N-arylsulphonyl (1) or other oxaziridines.

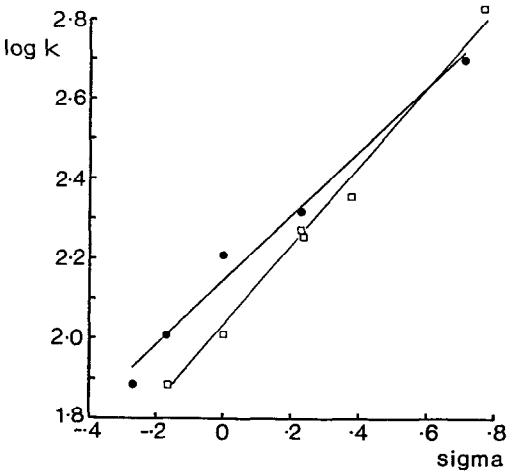
The second order kinetics here reported (first order in I^- and first order in oxaziridine) are, of course, consistent with rate determining attack of I^- on (1). Bimolecular nucleophilic ring-opening reactions of oxiranes and aziridines are well known, and generally proceed by attack at ring carbon with displacement of the electronegative heteroatom group. However, in the case of oxaziridines the displacement of a suitable nucleofuge may accompany attack by the nucleophile at either carbon, nitrogen or oxygen. Attack at carbon may proceed by C-N and/or C-O bond cleavage while attack at N or O would be expected to cause N-O bond breakage with displacement of oxygen or nitrogen, respectively.

In order to determine the distribution of charge within the transition

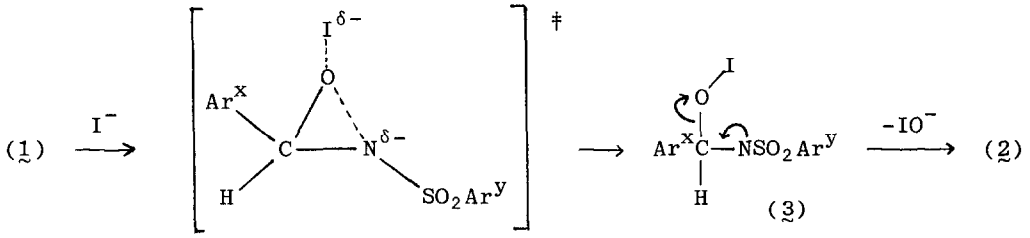
state for reaction of I^- with (1), and hence choose between the alternative mechanisms, we have correlated the rate constants (Table) with the Hammett substituent constants σ to obtain $\rho^X = 0.99$ (Y = p-Me, r = 0.997) and $\rho^Y = 0.81$ (X = H, r = 0.992), see Fig. below.

Hammett plots for reaction of oxaziridines (1) with iodide ion in 50% v/v $MeOH \cdot H_2O$ at 25°.

□ (1; X, p-Me), $\rho^X = 0.99$
● (1; H, Y), $\rho^Y = 0.81$



The excellent correlation with sigma and comparable positive rho values obtained suggest that the reaction proceeds by a single mechanism which probably features development of negative charge on an atom ca. equidistant from aryl rings Ar^X and Ar^Y. Consequently we favour a mechanism of nucleophilic attack on ring oxygen with concomitant O-N bond breakage (and elimination of IO^- from the ring opened product, in a subsequent fast step)



The degree of charge development on nitrogen can be gauged (only approximately, without knowledge of the Hammett relationship for equilibration of 1 and 3) by comparison with the known rho values for ionisation of sulphonamides $ArSO_2NH_2$ ($\rho = 1.06$)[9] and $ArSO_2NHPh$ ($\rho = 1.16$)[9], in water at 25°, if a correction is made ($\Delta\rho = 0.42$, see ref.10) for the change of solvent to 50% v/v methanol--water. Consequently we estimate that the incipient charge on nitrogen is ca. $-(0.81/1.53) = -0.53$. Furthermore, since there is evidence† to suggest that substituent effects are transmitted through sp^3-carbon slightly more readily than through sulphonyl sulphur, the value $\rho^X = 0.99$ is in reasonable agreement

with our interpretation of $\rho^y = 0.81$. Conversely, it is unlikely that there is significant positive or negative charge development on the electrophilic ring oxygen since this would cause a further decrease or increase in ρ^x relative to ρ^y; hence, our results are consistent with a transition state in which bond breaking leads bond making, with development of ca. -.53 esu of charge on nitrogen and a residual charge of ca. -0.47 on iodine.

Our observations find parallel in recent kinetic results[11] for reaction of tri-n-butylphosphine with 3-aryloxaziridines in hexane and in acetonitrile, for which the value $\rho = 1.06\text{-}1.12$ was interpreted in terms of displacement at oxygen rather than nucleophilic attack at carbon or nitrogen. The relatively few other mechanistic studies of oxaziridine ring-opening reactions have dealt only with acid catalysed hydrolyses and have revealed that competition between C-O and N-O bond breakage is markedly dependent upon the substitution pattern.[12-14]

† $\rho = 1.05$ for $ArCH_2NH_3^+ + H_2O \rightleftarrows ArCH_2NH_2 + H_2O$ (Ref.15)
$\rho = 0.88$ for $ArSO_2NH_3^+ + H_2O \rightleftarrows ArSO_2NH_2 + H_2O$ (Ref.16)

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(Received in UK 30 January 1984)