Base-catalysed Rearrangement of 2-Nitrobenzenesulphenanilides: an Intramolecular Oxygen Transfer Process

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RECENTLY, kinetic evidence for nucleophilic participation by *o*-nitro-groups has been presented.[1] We report an unequivocal demonstration, by using ^{18}O-labelled material, of such an interaction in the base-catalysed rearrangement of 2-nitrobenzenesulphenanilides, (I).

Cava and Blake[2] showed that (Ia) rearranges in hot aqueous alcoholic sodium hydroxide to give the azosulphinate, (IIa), and suggested a mechanism for this transformation involving oxygenation of the sulphur atom by attack of the hydroxide ion. However, the *X*-ray structural determination[3] of the related sulphenate ester, (III), which showed evidence for a strong interaction between the sulphur and one of the oxygen atoms of the nitro-group, prompted us to check on the origin of the oxygen atoms in (II).

Accordingly, rearrangement of (Ia) was carried out in aqueous alcoholic sodium hydroxide in which the H_2O and OH^- species contained 4·6 atom % excess ^{18}O. The product, (IIa), was isolated in good yield, and converted to the sulphone (IVa) [m.p. 94·5—96·5°, n.m.r. (CCl_4),§ δ 3·28 (s, 3H) and 7·4—8·2 p.p.m. (m, 9H); i.r. ($CHCl_3$), 1315 and 1150 cm.$^{-1}$]. Analysis of this material showed that it contained only (0·09 ± 0·04)% excess ^{18}O. This represents less than 2% of the incorporation required by the Cava mechanism, and clearly shows that *both* oxygens of (IIa) arise from the nitro-group.

The kinetics of the reaction were examined at 65° in 76% aqueous ethanol at several different hydroxide-ion concentrations between 0·1 and 0·5M, the ionic strength being kept constant with added sodium chloride. The reaction was found to obey the law, Rate = k_2[sulphenanilide][OH^-]. (A plot of pseudo-first order rate constants against [OH^-] was linear and passed through the origin.) A value of k_2 = (5·5 ± 0·1) × 10^{-3} l. mole^{-1} min.$^{-1}$ was obtained for (Ia). Similarly (Ib) rearranged to (IIb), characterised as the sulphone (IVb) [m.p. 105·5—106·5°; n.m.r. ($CDCl_3$), δ3·40 (s, 3H), 3·88 (s, 3H), and 6·9—8·4 p.p.m. (complex, 8H); i.r. ($CHCl_3$), 1320 and 1150 cm.$^{-1}$]. The rate constant, k_2, for

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§ N.m.r. spectra run at 60Hz with Me_4Si as internal reference.

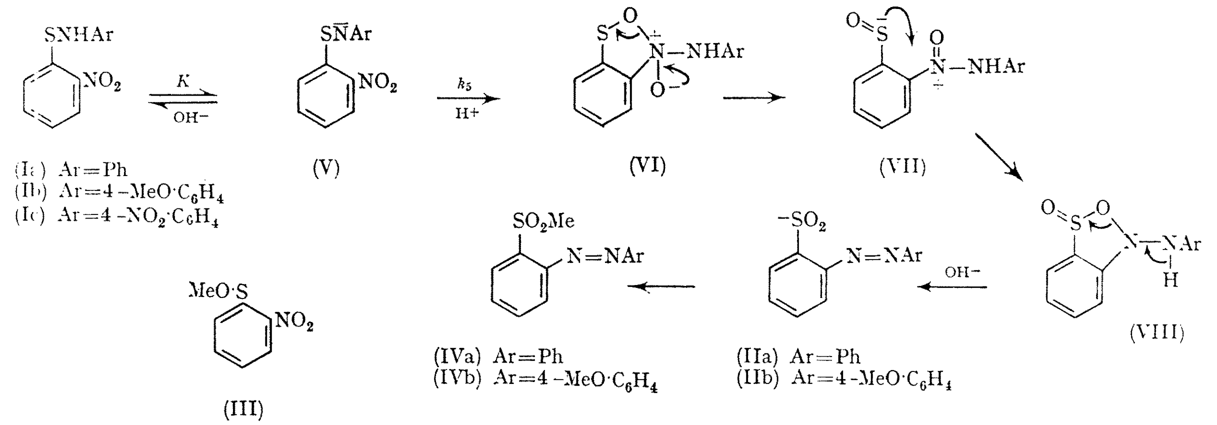

CHART 1

(Ib) was (14·2 ± 0·4) × 10^{-3} l. mole^{-1} min.^{-1}. However, when (Ic) was subjected to the same conditions, a 71% yield of 4-nitroaniline was obtained. We feel that these results are best accommodated by the following mechanism, in which k_5 is rate-limiting:

The observed rate constant k_2 will then be $K \times k_5$. When Ar = $4\text{-}CH_3O\cdot C_6H_4$, K will be smaller than when Ar = Ph, but k_5 will be larger. Apparently, the Hammett ρ-value for process (V) → (VI) is (numerically) greater than that for equilibration of (I) and (V), which gives rise to a small overall rate increase. When Ar = $4\text{-}NO_2\cdot C_6H_4$ the equilibrium will be shifted to the right, but k_5 will be considerably reduced. Simultaneously, the stability of $ArNH^-$ will be increased, facilitating the reaction (I) → $4\text{-}NO_2\cdot C_6H_4\cdot NH_2$, by direct attack of hydroxide on sulphenyl sulphur. Since, in the above mechanism, hydroxide is involved only in proton abstractions, it should be replaceable by any comparably strong base, and in fact (Ia) rearranges smoothly to (IIa) in dry alcoholic sodium ethoxide.

A possible route for the conversion of (V) to (VI) *via* a [2,1,1]bicyclic transition state[4] is shown on Chart 2.

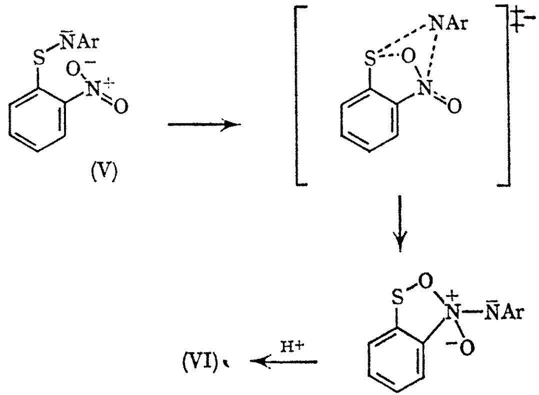

CHART 2

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