A Novel Use of Electron Spin Resonance Spectroscopy in the Detection of a Sigmatropic Rearrangement

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Summary The triethyl phosphite-induced conversion of [4-$^2H_1$]phenyl 2-nitrophenyl sulphide *via* a sigmatropic rearrangement into [3-$^2H_1$]phenothiazine has been demonstrated by e.s.r. spectroscopic examination of the cation radical of the latter.

THE existence of a rearrangement in the conversion, using triethyl phosphite, of aryl 2-nitrophenyl sulphides (I; $Y=NO_2$; X=Cl, Bu^t, Me, MeO *etc.*) and aryl 2-azidophenyl sulphides (I; $Y=N_3$; X=Cl, Me, Bu^t *etc.*), by thermolysis, into 3- rather than 2-substituted phenothiazines (II) has been recorded and a mechanism suggested (Scheme).[1] We have now used deuterium labelling to demonstrate that the rearrangement is general, involving, also, cases where the

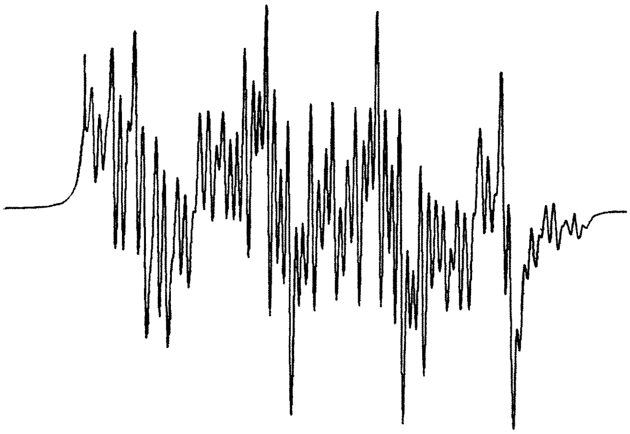


FIGURE 1

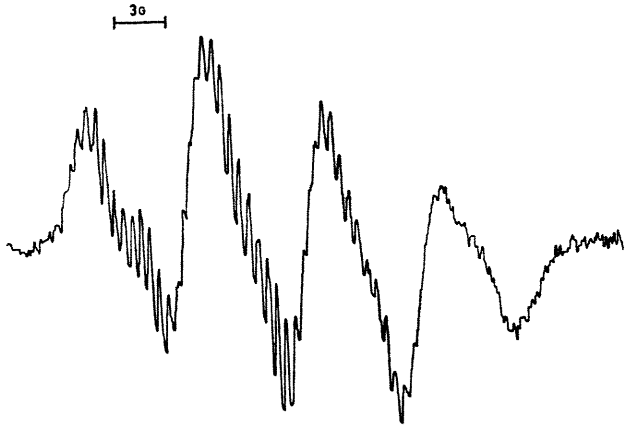


FIGURE 2

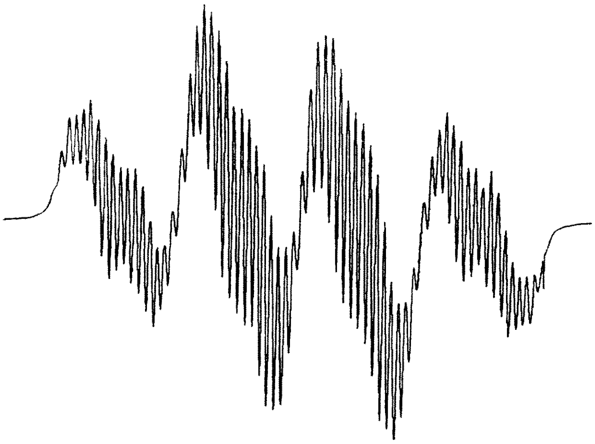
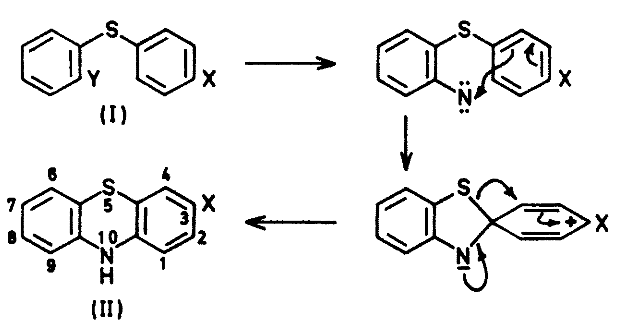


FIGURE 3

nitrene intermediate attacks an unsubstituted benzene ring (Scheme; X = D). Thus [4-$^{2}\mathrm{H}_1$]phenyl 2-nitrophenyl sulphide (monodeuterium content = 93% of theory), prepared unambiguously from 4-aminophenyl 2-nitrophenyl sulphide by the method of Renaud *et al.*,[2] on treatment with triethyl phosphite gave [$^{2}\mathrm{H}_1$]phenothiazine (54%; deuterium-content = 90% of theory). That this was the 3- and not the 2-deuterio-isomer follows unambiguously by comparison of the e.s.r. spectrum of the corresponding cation radical (Figure 2), produced in sulphuric acid (98%), with the computer simulations (line width 0·40 gauss)† corresponding to both isomers (Figures 1 and 3), produced using a modified programme QCPE 83 obtained from Quantum Chemistry Programme Exchange, with an IBM 360/44 computer and 1327 plotter. The assignment of structure is reinforced by comparison of the observed spectrum with that already reported for the corresponding phenothiazine cation radical.[3] The latter exhibits a quintet splitting with $a_2^{\mathrm{H}} = a_4^{\mathrm{H}} = a_6^{\mathrm{H}} = a_8^{\mathrm{H}} = 0{\cdot}46$ gauss which should collapse to a quartet with *a ca.* 0·46 gauss in the case of [2-$^{2}\mathrm{H}_1$]-phenothiazine and the resulting deuterium splitting of 0·46/6·5 = 0·07 gauss at position 2 will not be resolved, a situation observed in the simulated spectrum (Figure 3) but not in the spectrum of the product (Figure 2). Further, the phenothiazine cation radical exhibits a triplet ($a_3^{\mathrm{H}} = a_7^{\mathrm{H}} = 2{\cdot}58$ gauss) which in [3-$^{2}\mathrm{H}_1$]phenothiazine should be replaced by a doublet (a_7^{H} *ca.* 2·58 gauss) and a 1 : 1 : 1-deuterium triplet (a_3^{D} *ca.* 0·40 gauss). These appear in the spectrum simulated for [3-$^{2}\mathrm{H}_1$]phenothiazine cation radical (Figure 1), which is very similar to the experimental case (1 : 1 : 1-triplet a_3^{D} *ca.* 0·40 gauss) (Figure 2). E.s.r. spectra were recorded on a Decca X3 spectrometer using an 11 in. magnet (Newport Instruments) provided by means of an SRC research grant.



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† Chosen as the best line width in view of the experimentally observed variation of line width with field.

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[3] B. C. Gilbert, P. Hanson, R. O. C. Norman, and B. T. Sutcliffe, *Chem. Comm.*, 1966, 161; J. M. Lloste and F. Tannard, *J. Chim. phys.*, 1966, **63**, 678.