Oxygen Insertion into the Metal–Carbon Bond of Cyclopalladated 2-(Alkylsulphinyl)azobenzenes by Peracids. High Yield Regiospecific Aromatic Hydroxylation

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The title reaction occurs by an associative mechanism involving heterolytic O–O cleavage; the sequence azobenzene → (**1**) → (**2**) → azophenol leading to overall regiospecific aromatic hydroxylation has been realised.

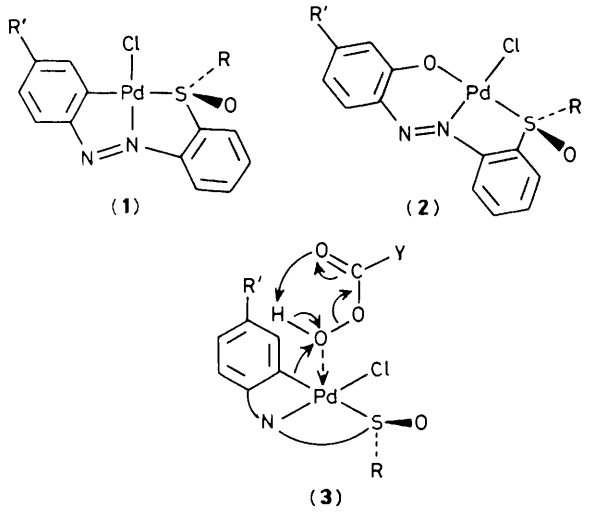
The insertion of oxygen into a metal–carbon σ-bond, M–C → M–OC, is a potentially useful tool for functionalisation of organic substrates. Thus the net result of the metallation–oxidation–demetallation sequence of equation (1) is hydroxylation. However, very little is known about the intermediate oxidation step.[1—3] We now report that the oxidation of cyclopalladated 2-(alkylsulphinyl) azobenzene (**1**) to the corresponding phenolato complex (**2**) by peracids (YCO_3H) is a clean, quantitative, and mechanistically tractable reaction. Smooth demetallation of (**2**) is achievable, resulting in high-yield aromatic hydroxylation according to the reaction sequence of equation (1).

$$C\text{–}H \rightarrow C\text{–}M \rightarrow C\text{–}OM \rightarrow C\text{–}OH \qquad (1)$$

To observe the effect of variation of R, R′, and Y on the rate of oxygen insertion, six reactions (r_1)—(r_6) were studied in chloroform solution (Table 1). Rates, monitored spectrophotometrically, are first order with respect to the concentrations of both (**1**) and YCO_3H. The spectra of the reaction

Table 1. Rate constants for oxygen insertion into cyclopallated 2-(alkylsulphinyl)azobenzenes (**1**) by peracids YCO_3H at 300 K in $CHCl_3$.

Reaction	R	R′	Y	k/mol^{-1} dm^3 s^{-1}
(r_1)	Me	H	$C_6H_4NO_2(p)$	1.86
(r_2)	Me	H	$C_6H_4Cl(m)$	0.41
(r_3)	Me	H	Ph	0.09
(r_4)	Me	H	$PhCH_2$	0.06
(r_5)	$PhCH_2$	H	$C_6H_4Cl(m)$	1.99
(r_6)	Me	Me	$C_6H_4Cl(m)$	0.69



solutions reveal that the only detectable palladium species present are (**1**) and (**2**) (Figure 1). Second order rate constants (300 K) are listed in Table 1. Variable temperature rate studies (289—307 K) made for (r_1)—(r_6) have revealed that the enthalpy of activation is uniformly small and positive (7—10 kcal mol^{-1}; 1 kcal = 4.184 kJ) and the entropy of activation is large and negative (−30 to −40 cal K^{-1} mol^{-1}). Clearly bond-breaking and bond-making are both important in a strongly associative transition state.

A plausible transition state is (**3**). The ability of palladium(II) to bind to peroxo oxygen has been documented.[4] The data of Table 1 reveal that the rate increases upon making (i) the Pd–C bond electron rich with the help of electron releasing R′ substitutents [*cf.* (r_2) and (r_6)], (ii) the Pd · · · O association in (**3**) stronger by augmenting the electrophilicity of the metal centre with the help of electron withdrawing R [*cf.* (r_2) and (r_5)], and (iii) YCO_2H a better leaving acid[5] by modifying Y [(r_1)—(r_4)]. The plot of log k *vs.* pK of YCO_2H is linear [(r_1)—(r_4)] and so is the plot of log k *vs.* Hammett σ of substituents (p-NO_2, m-Cl, and H) of aromatic acids [(r_1)—(r_3)] (Figure 2). The trends cited above strongly support the proposed electron movements in (**3**) which correspond to heterolytic O–O cleavage and electrophilic insertion of 'O' into the C–Pd bond.

In 3d metal ion catalysed epoxidation of alkenes by YCO_3H higher valent oxo complexes are demonstrable intermediates.[6] In contract we have no evidence for an intermediate oxo stage in the progression of (**3**) to (**2**) + YCO_2H. Oxometal species are expected[7] only when the number of d-electrons in the metal ion is ≤4. For palladium this condition is satisfied only by the unrealistic oxidation levels ≥+6. The electron movements in (**3**) are believed to be largely concerted.

The 2-(alkylsulphinyl)azobenzene ligands (LH) required for the synthesis of (**1**) were made by H_2O_2 (25%) oxidation of the corresponding sulphides in glacial acetic acid.[8] These

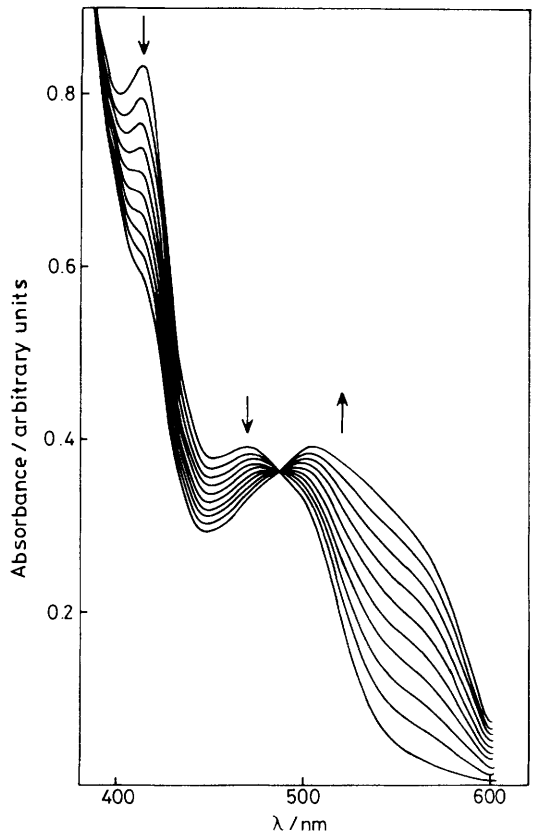


Figure 1. Visible spectra of a chloroform solution (300 K) in which reaction (r_4) is in progress. The arrows indicate increase and decrease of band intensities as the reaction proceeds.

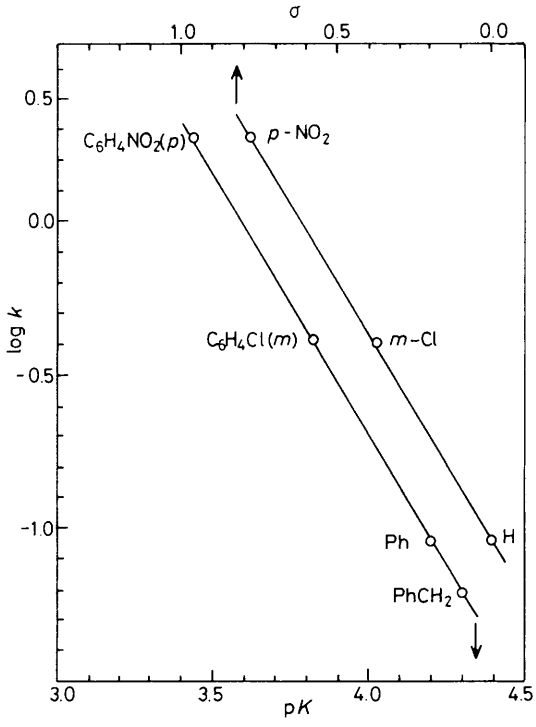


Figure 2. Hammett plots of log k *vs.* pK of YCO_2H (the Ys are indicated against corresponding points) and log k *vs.* Hammett σ of substituents of aromatic acids.

furnished deep brown (**1**) upon treatment of Na_2PdCl_4 in ethanol. The oxidation of (**1**) to dark violet (**2**) by YCO_3H occurs smoothly in chloroform solvent at room temperature. Complex (**2**) affords the corresponding free phenolic ligand (LOH) upon demetallation (metallic palladium is deposited) with hydrazine hydrate in acetonitrile. The regiospecific (*ortho* to azo function) hydroxylation of LH to LOH is thus accomplished. The yields for all three steps [LH → (**1**) → (**2**) → LOH] are excellent (80—100%). All ligands and complexes are new and were characterized with the help of elemental analysis, i.r., u.v.–visible, and high-resolution ^1H n.m.r. spectra.[9] For most species the ^1H n.m.r. signals for all protons could be unambiguously assigned. The S-binding of 2-(alkylsulphinyl)azobenzenes is reflected[10] in the downfield shift of the R signals in going from ligand to complex [δ_{Me}: (**1**; R = Me, R′ = H) 3.41; ligand 2.91] and the increase in methylene proton inequivalence [δ_{CH_2} ($J \sim 13$ Hz): (**1**; R = CH_2Ph, R′ = H) 4.62, 5.02; ligand 4.12, 4.34]. Also the SO stretch in the i.r. is blue-shifted[11] upon complexation (complexes 1110—1150; ligands 1030—1040 cm^{-1}). Identification of (**2**) was completed by independent synthesis from ligands generated authentically *via* nonoxidative routes (diazo coupling).[9]

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References

1 I. J. Harvie and F. J. McQuillin, *J. Chem. Soc., Chem. Commun.*, 1976, 369; B. A. Grigor and A. Neilson, *J. Organomet. Chem.*, 1977, **129**, C17.
2 A. K. Mahapatra, D. Bandyopadhyay, P. Bandyopadhyay, and A. Chakravorty, *Inorg. Chem.*, 1986, **25**, 2214; A. K. Mahapatra, D. Bandyopadhyay, P. Bandyopadhyay, and A. Chakravorty, *J. Chem. Soc., Chem. Commun.*, 1984, 999.
3 A. V. Assett, B. D. Santarsiero, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1986, **108**, 8291; T. V. Lubben and P. T. Wolczanski, *ibid.*, 1985, **107**, 701.
4 H. Mimoun, R. Charpentier, A. Mitschler, J. Fischer, and R. Weiss, *J. Am. Chem. Soc.*, 1980, **102**, 1047.
5 W. A. Lee and T. C. Bruice, *Inorg. Chem.*, 1986, **25**, 131.
6 J. T. Groves, R. C. Haushalter, N. Nakamura, T. E. Nemo, and B. J. Evans, *J. Am. Chem. Soc.*, 1981, **103**, 2884; T. G. Traylor and A. R. Miksztal, *ibid.*, 1987, **109**, 2770; A. Selvin and M. Fontecave, *ibid.*, 1986, **108**, 3266, and references therein.
7 R. H. Holm, *Chem. Rev.*, 1987, **87**, 1401.
8 E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 1927, 1798; D. S. Tarbell and C. Weaver, *J. Am. Chem. Soc.*, 1941, **63**, 2939.
9 C. R. Sinha, D. Bandyopadhyay, and A. Chakravorty, *Inorg. Chem.*, 1988, in the press.
10 J. A. Davies, *Adv. Inorg. Chem. Radiochem.*, 1981, **24**, 115; W. Kitching, C. J. Moore, and D. Doddrell, *Aust. J. Chem.*, 1969, **22**, 1149.
11 J. H. Price, A. N. Williamson, R. F. Schramm, and B. B. Wayland, *Inorg. Chem.*, 1972, **11**, 1280; W. Kitching, C. J. Moore, and D. Doddrell, *ibid.*, 1970, **9**, 541.