Applicability and mathematical verification of the reactivity–selectivity principle in the oxidation of thioanisoles by oxo(salen)manganese(V) complexes†

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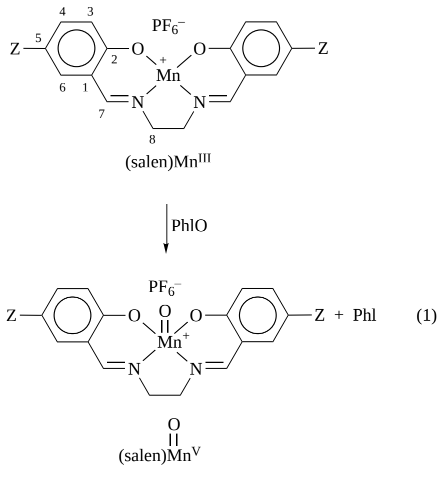
The second-order rate constants for the oxidation of various *para*-substituted thioanisoles with substituted oxo(salen)manganese(V) complexes have been measured spectrophotometrically in acetonitrile at 25 °C. Electron-withdrawing substituents in thioanisoles and electron-releasing substituents in oxo(salen)Mn^V complexes decrease the rate of oxidation. Correlation analyses show the presence of an inverse relationship between reactivity and selectivity in the reactions of various thioanisoles with a given oxo(salen)Mn^V complex and also in various oxo(salen)Mn^V complexes with a given thioanisole. Mathematical treatment of the results has also been carried out.

The validity of the concept that there is an inverse relationship between the reactivity of a reagent and its selectivity among a set of similar substrates, known as the reactivity–selectivity principle (RSP), has recently been subjected to critical analysis.[1–4] RSP has been tested with hydration, acid–base catalysis, solvolysis, oxidation, reduction and other types of reaction.[3–6] However, applicability of RSP to biologically relevant oxygen atom transfer (oxygenation) reactions has not yet been reported. Oxygenation reactions[7–9] have long been targets for antibody catalysis as they mimic the metabolic activity of biological enzymes[10] such as cytochrome P-450 and xanthine oxidase. Metal–porphyrin[11] and metal–salen[12–20] complexes have been used to catalyse oxidation of alkenes,[12–16] alkynes[17] and sulfides[18–20] by monooxygen atom donors, *viz.* PhIO,[15–19] H_2O_2,[14,20] hypochlorite[12] or periodate.[13]

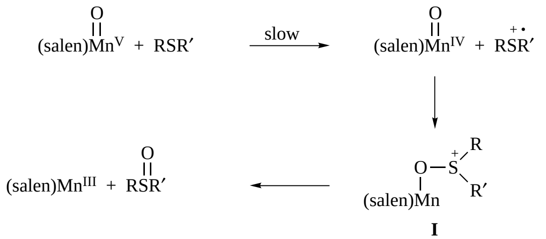
Recently, we have investigated the oxidation of organic sulfides by oxo(salen)manganese(V)[18] and oxo(salen)chromium(V)[19] complexes. Herein we report our results on the applicability of RSP to the oxidation of aryl methyl sulfides by oxo(salen)manganese(V) complexes **1**–**4** (hereafter referred to as oxo complexes) generated *in situ* from the corresponding [Mn^{III}(salen)]$^+$PF$_6^-$ complexes and PhIO as represented in eqn. (1).



1 Z = OMe
2 Z = H
3 Z = Cl
4 Z = NO$_2$

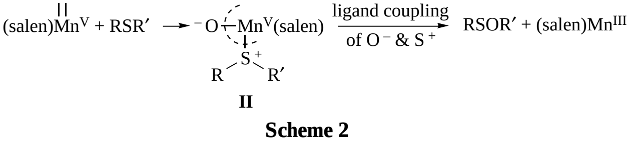
Results and discussion

The kinetics of oxygen atom transfer from oxomanganese(V) complexes **1**–**4** to various *para*-substituted thioanisoles has been studied spectrophotometrically in acetonitrile at 25 °C. The reaction is second-order overall, first-order each in the complex and the substrate, which is evident from the k_1 and k_2 values reported in Table 1 for the reaction of methyl phenyl sulfide (MPS) with the oxo complexes **1**–**4**. A single electron transfer (SET) mechanism[18] leading to the formation of a cation radical in the slow step has been proposed. The intermediate **1** decomposes to give LMn^{III} and sulfoxide as the products in a fast step (Scheme 1). The postulation of this mechanism is supported by the study of substituent effects and the comparison of experimental rate constants with the rate constant calculated from the Marcus theory of electron transfer.



Scheme 1

In an alternative mechanism[18] (Scheme 2), the formation of a hypervalent intermediate **II** either in a single step due to electrophilic attack of Mn on the sulfide sulfur or in two single electron transfer steps has been discussed. Sulfoxide is



Scheme 2

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† H_2salen = *N*,*N*′-Bissalicylideneethylenediamine.

Table 1 Rate constants for the oxidation of MPS by oxo complexes **1-4** in acetonitrile at 25 °C [a]

[MPS]/ 10^{-2} M	[Mn^{V}]/ 10^{-3} M	$k_{1(obs)}$ [b]/ 10^{-4} s^{-1}	$k_{1(dec)}$ [c]/ 10^{-4} s^{-1}	k_1 [d]/ 10^{-4} s^{-1}	k_2 [e]/ 10^{-3} dm^3 mol^{-1} s^{-1}
	1				
10.0	1.80	8.27 ± 0.23	3.90 ± 0.17	4.37 ± 0.06	4.37 ± 0.16
20.0	1.80	12.6 ± 0.5	3.90 ± 0.17	8.70 ± 0.33	4.35 ± 0.17
50.0	1.80	25.1 ± 1.2	3.90 ± 0.17	21.2 ± 1.0	4.24 ± 0.20
75.0	1.80	34.3 ± 2.9	3.90 ± 0.17	30.4 ± 2.7	4.05 ± 0.36
100.0	1.80	45.8 ± 2.5	3.90 ± 0.17	41.9 ± 2.3	4.19 ± 0.23
	2 [f]				
4.0	0.83	7.79 ± 0.38	5.27 ± 0.44	2.52 ± 0.06	6.30 ± 0.15
4.0	1.24	7.69 ± 0.37	5.23 ± 0.24	2.46 ± 0.13	6.15 ± 0.33
4.0	1.65	7.32 ± 0.58	4.72 ± 0.29	2.60 ± 0.29	6.50 ± 0.73
4.0	1.80	7.47 ± 0.42	4.84 ± 0.32	2.63 ± 0.10	6.58 ± 0.25
4.0	3.04	7.73 ± 0.45	5.05 ± 0.19	2.68 ± 0.26	6.70 ± 0.65
10.0	1.80	11.2 ± 0.8	4.84 ± 0.32	6.37 ± 0.48	6.37 ± 0.48
14.0	1.80	13.7 ± 0.9	4.84 ± 0.32	9.12 ± 0.58	6.51 ± 0.41
20.0	1.80	18.2 ± 1.1	4.84 ± 0.32	13.4 ± 0.8	6.70 ± 0.39
50.0	1.80	36.2 ± 3.8	4.84 ± 0.32	31.4 ± 3.5	6.27 ± 0.70
100.0	1.80	67.7 ± 6.5	4.84 ± 0.32	62.9 ± 6.2	6.29 ± 0.62
	3				
2.0	1.80	7.92 ± 0.62	5.08 ± 0.42	2.84 ± 0.20	14.2 ± 1.0
5.0	1.80	11.9 ± 0.9	5.08 ± 0.42	6.82 ± 0.48	13.6 ± 1.0
10.0	1.80	19.8 ± 1.7	5.08 ± 0.42	14.7 ± 1.3	14.7 ± 1.3
15.0	1.80	26.5 ± 1.5	5.08 ± 0.42	21.4 ± 1.1	14.3 ± 0.7
20.0	1.80	32.9 ± 2.4	5.08 ± 0.42	27.8 ± 2.0	13.9 ± 1.0
	4				
2.0	1.80	13.3 ± 0.7	5.15 ± 0.32	8.15 ± 0.38	40.8 ± 1.9
5.0	1.80	24.1 ± 1.0	5.15 ± 0.32	19.0 ± 0.7	38.0 ± 1.4
10.0	1.80	45.6 ± 1.7	5.15 ± 0.32	40.5 ± 1.4	40.5 ± 1.4
15.0	1.80	61.7 ± 1.6	5.15 ± 0.32	56.6 ± 1.3	37.7 ± 0.9
20.0	1.80	86.7 ± 6.5	5.15 ± 0.32	81.6 ± 6.2	40.8 ± 3.1

[a] As determined by a spectrophotometric technique following the disappearance of oxo complex at 680 nm; the error quoted in k values is the 95% confidence limit of Student's t test.[21] [b] Estimated from pseudo-first-order plots over 20% reaction. [c] Estimated from first-order plots over 50-60% reaction in the absence of sulfide. [d] Obtained as $k_1 = k_{1(obs)} - k_{1(dec)}$. [e] Individual k_2 values estimated as k_1/[S]. [f] Data taken from ref. 18.

Table 2 Second-order rate constants and ρ values for the reactions of *para*-substituted thioanisoles (p-XC_6H_4SMe) with substituted oxo complexes in acetonitrile at 25 °C [a,b]

	Oxo complex $k_2/10^{-3}$ dm^3 mol^{-1} s^{-1}					
X	Z = OMe	H	Cl	NO_2	ρ [d]	(r)
OMe	22.8 ± 2.1	26.4 ± 1.6	36.4 ± 2.5	52.0 ± 3.1	0.176 ± 0.042	(0.988)
Me	9.25 ± 0.40	12.0 ± 0.8	21.7 ± 1.7	43.6 ± 1.8	0.332 ± 0.075	(0.989)
H	4.37 ± 0.18	6.70 ± 0.39	14.2 ± 1.0	40.8 ± 3.1	0.474 ± 0.078	(0.994)
F	3.27 ± 0.23	4.89 ± 0.12	11.6 ± 0.2	30.6 ± 1.5	0.477 ± 0.110	(0.989)
Cl	1.73 ± 0.12	2.67 ± 0.29	8.38 ± 0.38	19.0 ± 1.4	0.515 ± 0.192	(0.971)
Br	1.48 ± 0.17	2.50 ± 0.11	7.36 ± 0.41	17.1 ± 0.2	0.520 ± 0.177	(0.976)
CO_2H [c]	0.74 ± 0.11	1.28 ± 0.15	3.46 ± 0.03	9.15 ± 0.12	0.532 ± 0.141	(0.985)
COMe	0.40 ± 0.06	0.71 ± 0.08	2.34 ± 0.04	4.91 ± 0.25	0.533 ± 0.219	(0.965)
NO_2	0.12 ± 0.03	0.24 ± 0.04	0.78 ± 0.08	1.65 ± 0.03	0.554 ± 0.228	(0.964)
ρ [e]	−2.06 ± 0.19	−1.85 ± 0.16	−1.52 ± 0.18	−1.44 ± 0.32		
(r)	(0.995)	(0.995)	(0.992)	(0.970)		

[a] The errors quoted in k_2 is 95% CL of the 'Student t'.[21] [b] General conditions: [oxo complex] = 0.0018 M; [sulfide] = 0.2 M. [c] [sulfide] = 0.1 M. [d] The values were obtained by correlating log k_2 with $2\sigma_p$ for the reaction of various oxo complexes with a given thioanisole. [e] The values were obtained by correlating log k_2 with σ_p for the reaction of various thioanisoles with a given oxo complex.

formed due to ligand coupling of S^+ and O^- in the intermediate **II**.‡

The second-order rate constants for the reactions of various *para*-substituted thioanisoles with each of the oxo complexes are listed in Table 2. The rate data in Table 2 show that introduction of substituents in the oxidant and the substrate has the opposite effect on the rate of reaction *i.e.* electron-releasing substituents in the oxo complex as well as electron-withdrawing substituents in the sulfide retard the rate of oxidation. The kinetic data for the reactions of various thioanisoles with a given oxo complex and various oxo complexes with a given sulfide have been correlated with Hammett substituent constants. The correlation is better with σ_p values rather than with σ^+/σ^- values. A better correlation of log k_2 with σ^+ or σ^- values rather than with σ values has been postulated earlier for an electron-transfer mechanism[26,27] for the oxidation of organic sulfides. However, Miller *et al.*[28] have cautioned against deciding a reaction mechanism simply based on the correlation of log k with σ^+/σ^- or on the magnitude of ρ value. Thus the correlation of log k with σ^+/

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‡ One of the referees suggested another possibility of a direct oxygen transfer from the oxo complex to sulfur without the formation of an intermediate. But we have not considered this aspect as the dialkyl sulfides are oxidized much more slowly than thioanisoles (*cf.* ref. 18), which is in favour of SET and against direct oxygen transfer. A similar explanation has been offered in the Ce^{IV} oxidation of organic sulfides.[22] Further, for the reactions where a larger reactivity of dialkyl sulfides compared to thioanisole has been observed, a direct oxygen transfer mechanism has been suggested.[23–25]

Table 3 Results of correlation between log $k_{\mathrm{F}i}$ and log $k_{\mathrm{S}i}$ according to eqn. (2)

	Oxo complexes (F and S)					
Results	**2** and **1**	**3** and **1**	**3** and **2**	**4** and **1**	**4** and **2**	**4** and **3**
r	0.999	0.992	0.993	0.963	0.969	0.985
b	0.900 ± 0.022	0.733 ± 0.085	0.816 ± 0.084	0.689 ± 0.172	0.770 ± 0.177	0.954 ± 0.149
Δ	0.194	0.585	0.392	0.933	0.739	0.348

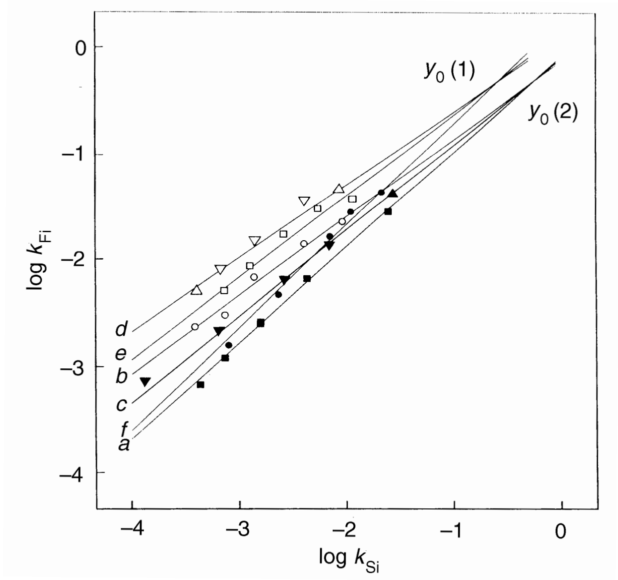

Fig. 1 Log $k_{\mathrm{F}i}$ *vs.* log $k_{\mathrm{S}i}$ plots for the reactions of substituted thioanisoles with (*a*) **2** and **1**, (*b*) **3** and **1**, (*c*) **3** and **2**, (*d*) **4** and **1**, (*e*) **4** and **2** and (*f*) **4** and **3** (for clarity, only five points are shown for each line)

σ^- is not a necessary condition for the proposal of an electron transfer mechanism.§ It is pertinent to point out here that a good correlation of log k with σ has been observed in the $\mathrm{Cr^{VI}}$ oxidation of organic sulfides[29] where a SET mechanism has been established.

The last row of Table 2 contains ρ values for substituent variation in thioanisole for each oxo complex while the last column shows reaction constants for substituent variation in oxo complex for each thioanisole. The ρ values in Table 2 show that there is a significant variation of reaction constants (selectivity) when we vary the nature of substituent either in the oxo complex or in the sulfide. Also, it is apparent that as the reactivity of either sulfide or oxo complex decreases the ρ value increases *i.e.* there is an inverse relationship between reactivity and selectivity in both cases. However, the ρ values shown in the last column of Table 2 deserve an explanation. Though it changes significantly when *p*-OMe is introduced in place of H, little change is observed if *p*-$\mathrm{NO_2}$ is substituted. We have used only four points in the correlation of log k_2 *vs.* 2σ and the r values observed in the case of sulfides containing electron-withdrawing groups (except *p*-F and *p*-$\mathrm{CO_2H}$) are only satisfactory. Further, the error associated with ρ values for these sulfides is high compared to that observed for sulfides having electron-releasing groups. Thus the ρ value measured for *p*-$\mathrm{NO_2C_6H_4SMe}$ is less reliable compared to that for *p*-$\mathrm{OMeC_6H_4SMe}$.

Mathematical verification

When two reagents (fast F and slow S) and a series of similar substrates ($i = 1, 2 \ldots n$) can be chosen in such a way that the greatest difference in reactivity within the substrate set is greater than between the reagents the RSP then requires a more or less precise linear relationship[4] between the two series, as in eqn. (2)

$$\log k_{\mathrm{F}i} = a + b \log k_{\mathrm{S}i} + \varepsilon_i \qquad (2)$$

where $k_{\mathrm{F}i}$ and $k_{\mathrm{S}i}$ are the second-order rate constants for the reactions of fast and slow reagents (oxo complexes) respectively with each sulfide and ε_i is the error of the log $k_{\mathrm{F}i}$ *vs.* log $k_{\mathrm{S}i}$ correlation. Since the difference between the reagents is variable along the series of substrates, the mean difference Δ can be calculated using eqn. (3).

$$\Delta = \left(\sum_i \log k_{\mathrm{F}i} - \sum_i \log k_{\mathrm{S}i}\right)/N \qquad (3)$$

Based on the values of b and Δ, four types of RSP have been discussed.[4] (*i*) A valid RSP [RSP(+)] when $b < 1$ and Δ is not too small. (*ii*) Anti-RSP [RSP(−)] when $b > 1$. (*iii*) Indifferent behaviour [RSP(?)] when $b = 1$. (*iv*) A cross-over RSP *i.e.* RSP is valid in one part of the series and invalid in the other [RSP(±)] when Δ is too small.

With the rate data available in Table 2, log $k_{\mathrm{F}i}$ values were plotted against log $k_{\mathrm{S}i}$ values according to eqn. (2) to find slope b and the values of Δ were calculated using eqn. (3) for all the six possible combinations of one fast and one slow reagent (among the four oxo complexes) with a series of similar substrates (nine thioanisoles) (Fig. 1). The results summarized in Table 3 show a valid RSP in all cases as the value of b is less than unity and Δ is not too small.

In a system involving more than one reagent and the same set of substrates, the existence of a 'magic point'[4] in the log $k_{\mathrm{F}i}$ *vs.* log $k_{\mathrm{S}i}$ plots is an indication for a strong RSP. The magic point represents some limiting value of reactivity in which, for a particular substrate, the reaction rate is independent of the reagent and *vice versa*. In this aspect, the present system reveals interesting results (Fig. 1). The correlations involving nitro-substituted oxo complex **4** (lines *d*–*f*) produce one magic point, $y_0(1)$ and the correlations involving other oxo complexes (lines *a*–*c*) produce another magic point, $y_0(2)$. Both magic points are situated on the side of high reactivity, as expected for a strong RSP as observed in the solvolysis[4,30] of various *meta*- and *para*-substituted allyl benzenesulfonates with various alcohols. Also, it can be seen from Table 3 (the last three columns) that the correlations involving **4** have b values with high error (>10%). Hence, the reason for the different behaviour of **4** may be an insufficiently precise linearity, rather than chemical differences between the reagents.

In a detailed analysis of RSP, Exner[4] has concluded that although RSP was evidently disproved as a general rule, investigations of selectivity and its relation to reactivity should be continued and used possibly to characterise a certain type of reaction or a certain mechanism. The operation of RSP has been attributed to the factors[3,5] that (*i*) absence of solvent effects, (*ii*) no appreciable structural change near the reaction site, and (*iii*) no change in mechanisms. Hence, the fact that the present system obeys RSP may be considered as evidence that the same mechanism is operating in all reactions.

Experimental

All the thioanisoles were prepared according to the reported procedure.[31,32] The purity of the sulfides was checked by HPLC analyses which showed the presence of a single entity in each sulfide. Acetonitrile (GR, E. Merck) was first refluxed over $\mathrm{P_2O_5}$ for 5 h and then distilled. Iodosylbenzene was prepared from (diacetoxyiodo)benzene by a standard method.[33]

The $[\mathrm{Mn^{III}(salen)}]^+\mathrm{PF_6}^-$ complexes were synthesised accord-

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§ For a detailed discussion on the mechanism see ref. 18.

ing to a known procedure.[16,18] The IR and UV–VIS spectral studies of all the complexes were found to be identical with literature data.[16] The oxo complexes **1**–**4** were generated[18] *in situ* by stirring magnetically 0.15 mmol of finely powdered PhIO in 5 ml acetonitrile solution containing 0.015 mmol of corresponding $\mathrm{Mn^{III}}$(salen) complex for 5 min under nitrogen followed by filtration at ice temperature to remove the undissolved iodosylbenzene. The conversion of $\mathrm{Mn^{III}}$ to $\mathrm{Mn^{V}}$ may be considered quantitative in the sense that prolonged stirring causes no change in the initial absorption spectrum of $\mathrm{Mn^{V}}$ solution.

Kinetic measurements

Reaction mixtures for kinetic runs were prepared by quickly mixing the solutions of the oxo complex and sulfide in varying volumes so that in each run the total volume was 5 ml. The kinetics was followed in a Perkin-Elmer UV–VIS spectrophotometer (Lambda 3B) fitted with thermostatted cell compartments under pseudo-first-order conditions ([sulfide] > [oxo complex]) in acetonitrile at 25 ± 0.1 °C by monitoring the decay of oxo complex at 680 nm.[16,18]

The rate constants were computed from the linear least-squares plots of $\ln(A_t - A_\infty)$ *vs.* time, where A_t is the absorbance at time t and A_∞ is the experimentally determined infinity point. The values of k_1 were obtained[18,23] as $k_1 = k_{1(\mathrm{obs})} - k_{1(\mathrm{dec})}$ where $k_{1(\mathrm{dec})}$ represents the first-order rate constants for the auto-decomposition of oxo complex and $k_{1(\mathrm{obs})}$ represents the pseudo-first-order rate constants for the decay of oxo complex in the presence of sulfides. The second-order rate constants, k_2, were obtained by the relation $k_2 = k_1/[\mathrm{sulfide}]$.

The reaction mixture from an actual kinetic run was subjected to vacuum evaporation and the residue was then extracted with diethyl ether. The ethereal extract was dried over anhydrous $\mathrm{Na_2SO_4}$ and the solvent evaporated. The product was dissolved in $\mathrm{CH_2Cl_2}$ and the GC analyses of the samples showed the presence of sulfoxide and iodobenzene. The yield of sulfoxide (60–70%) depended on the sulfide and oxo complex employed. The lower yield of sulfoxide may be attributed to the competitive self-decomposition of oxomanganese(V) complex to $\mathrm{Mn^{III}}$ complex, which is confirmed by the near quantitative recovery of $\mathrm{Mn^{III}}$ complex from the reaction mixture.

The reaction carried out under stoichiometric conditions ([**2**] = 0.0018 M; [PhSMe] = 0.018 M) gave sulfoxide in *ca.* 70% yield and $\mathrm{Mn^{III}}$ (salen) complex in *ca.* 95% yield with negligible amount of sulfone. Accordingly, the stoichiometry for the oxidation of sulfides with oxo complexes can be represented by eqn. (4).

$$\mathrm{O{=}Mn^{V}(salen)^{+} + PhSMe \longrightarrow Mn^{III}(salen)^{+} + PhSOMe} \qquad (4)$$

Ando and co-workers[34,35] have reported the direct oxidation of sulfides by PhIO in $\mathrm{CH_2Cl_2}$. To check whether there is any reaction between the dissolved PhIO and sulfide under the present experimental conditions we have carried out the reaction as described below. A solution of PhIO was prepared by stirring 33 mg (0.15 mmol) of finely powdered PhIO in 5 ml of acetonitrile for 5 min followed by filtration. The concentration of PhIO in the solution was too low to be detected by iodometric estimation (the solubility of PhIO in acetonitrile[16] is very low, 10^{-4} mM). To the PhIO solution thus prepared *ca.* 0.2 M MPS was added and the product analyses showed negligible amount of sulfoxide. This experimental observation led us to conclude that the reported sulfoxide yield is mainly due to the reaction between oxo complex and sulfide.

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References

1 C. D. Johnson, *Chem. Rev.*, 1975, **75**, 755.
2 A. Pross, *Adv. Phys. Org. Chem.*, 1977, **14**, 69.
3 C. D. Johnson, *Tetrahedron*, 1980, **36**, 3461 and references cited therein.
4 O. Exner, *J. Chem. Soc., Perkin Trans. 2*, 1993, 973.
5 (*a*) C. Srinivasan, P. Kuthalingam and N. Arumugam, *J. Chem. Soc., Perkin Trans. 2*, 1980, 170; (*b*) D. Bethell, A. E. Graham, J. P. Heer, O. Markopoulou, P. C. B. Page and B. K. Park, *J. Chem. Soc., Perkin Trans. 2*, 1993, 2161; (*c*) I. Lee, H. J. Koh, Y. S. Park and H. W. Lee, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1575.
6 E. Buncel and C. J. Chanqui, *J. Org. Chem.*, 1980, **45**, 2825.
7 R. H. Holm, *Chem. Rev.*, 1987, **87**, 1401.
8 B. Meunier, *Chem. Rev.*, 1992, **92**, 1411.
9 R. S. Drago, *Coord. Chem. Rev.*, 1992, **117**, 185.
10 (*a*) R. Sato and Y. Omuru, *Cytochrome P-450*, Kodansa, Tokyo and Academic Press, New York, 1980; (*b*) H. L. Holland, *Chem. Rev.*, 1988, **88**, 473; (*c*) A. G. Cochran and P. G. Schultz, *J. Am. Chem. Soc.*, 1990, **112**, 9414; (*d*) M. H. Gelb, W. A. Toscano, Jr., and S. C. Sligar, *Proc. Natl. Acad. Sci.*, 1982, **79**, 5758; (*e*) J. Amesz, *Biochim. Biophys. Acta*, 1983, **1**, 726.
11 (*a*) E. Guilmet and B. Meunier, *Tetrahedron Lett.*, 1982, **23**, 2449; (*b*) 1980, **21**, 4449; (*c*) J. T. Groves and M. K. Stern, *J. Am. Chem. Soc.*, 1988, **110**, 8628; (*d*) P. L. Anelli, S. Banfi, F. Montanari and S. Quici, *J. Chem. Soc., Chem. Commun.*, 1989, 779.
12 W. Zhang and E. N. Jacobsen, *J. Org. Chem.*, 1991, **56**, 2296.
13 P. Pietikainen, *Tetrahedron Lett.*, 1995, **36**, 319.
14 P. Pietikainen, *Tetrahedron Lett.*, 1994, **35**, 941.
15 E. G. Samsel, K. Srinivasan and J. K. Kochi, *J. Am. Chem. Soc.*, 1985, **107**, 7606.
16 K. Srinivasan, P. Michuad and J. K. Kochi, *J. Am. Chem. Soc.*, 1986, **108**, 2309.
17 B. Rihter, S. SriHari, S. Hunter and J. Masnovi, *J. Am. Chem. Soc.*, 1993, **115**, 3918.
18 A. Chellamani, N. M. I. Alhaji, S. Rajagopal, R. Sevvel and C. Srinivasan, *Tetrahedron*, 1995, **51**, 12677.
19 R. Sevvel, S. Rajagopal, C. Srinivasan, N. M. I. Alhaji and A. Chellamani, submitted for publication.
20 M. Palucki, P. Hanson and E. N. Jacobsen, *Tetrahedron Lett.*. 1992, **33**, 7111.
21 C. Srinivasan, S. Rajagopal and A. Chellamani, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1839.
22 E. Baciocchi, D. Intini, A. Piermattei, C. Roe and B. Ruzziconi, *Gazz. Chim. Ital.*, 1989, **119**, 646.
23 R. Curci, S. Giannattasio, O. Sciacovelli and L. Troisi, *Tetrahedron*, 1984, **40**, 2763.
24 F. Ruff and A. Kucsman, *J. Chem. Soc., Perkin Trans. 2*, 1985, 683.
25 H. G. Hanthal, H. Onderka and W. Pritzkow, *J. Prakt. Chem.*, 1969, **82**, 311.
26 (*a*) S. Oae, Y. Watanabe and K. Fujimori, *Tetrahedron Lett.*, 1982, 1189; (*b*) Y. Watanabe, T. Numata, T. Iyanagi and S. Oae, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1163.
27 J. H. Acquaye, J. G. Muller and K. J. Takeuchi, *Inorg. Chem.*, 1993, **32**, 160.
28 A. E. Miller, J. J. Bischoff, C. Bizub, P. Luminoso and S. Smiley, *J. Am. Chem. Soc.*, 1986, **108**, 7773.
29 C. Srinivasan, A. Chellamani and S. Rajagopal, *J. Org. Chem.*, 1985, **50**, 1201.
30 R. V. Sendega, R. V. Vizgert and M. K. Mikhalevich, *Reakts. Sposobnost Org. Soedin.* (*Tartu*), 1970, **7**, 512.
31 H. Zahn and H. Zuber, *Chem. Ber.*, 1953, **86**, 180.
32 V. Baliah and M. Uma, *Tetrahedron*, 1963, **19**, 455.
33 H. Saltzman and J. G. Sharefkin, *Organic Syntheses*, Vol. V, New York, Wiley, 1973, 658.
34 T. Takata, R. Tajima and W. Ando, *Phosphorous and Sulfur*, 1983, **16**, 67.
35 W. Ando, R. Tajima and T. Takata, *Tetrahedron Lett.*, 1982, **23**, 1685.

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