# The reactivity–selectivity principle in the oxidation of aryl methyl sulfides with sodium hypochlorite catalysed by (salen)Mn$^{III}$ complexes

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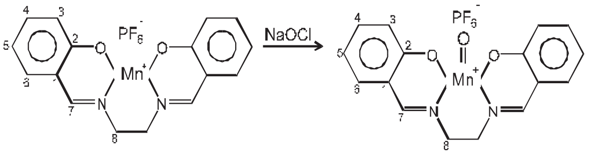
The kinetics of oxygen atom transfer from four oxo(salen)manganese(V) complexes to various *para*-substituted phenyl methyl sulfides have been studied spectrophotometrically in 90% acetonitrile-10% water(v/v) at 20°C. Electron-releasing substituents in sulfides and electron-withdrawing substituents in oxo(salen)manganese(V) complexes enhance the rate of oxidation. Correlation analyses establish that there is an inverse relationship between reactivity and selectivity in both the sulfide and the complex series. Mathematical treatment of the results shows the operation of a valid reactivity-selectivity principle in this redox system.

The Reactivity-Selectivity Principle (RSP), applies when there is an inverse relationship between the reactivity of a reagent and its selectivity among a set of similar substrates. Its validity has been a subject of much critical analysis.[1-4] RSP has been tested in hydration, acid–base catalysis, solvolysis, oxidation and reduction and other types of reaction.[3-9] However, many groups of workers[3,10,11] have questioned the validity of RSP and suggested that the use of RSP as a tool for the prediction or interpretation of reactions be discontinued. Buncel and Wilson,[12] from a critical analysis, concluded that the RSP represents an oversimplification but can be considered a rather special case. Exner[4] redefined this principle in terms of simple mathematical expressions, involving only rate constants and avoiding any $\sigma$ constants, equilibrium constants or other parameters. From the statistical analysis of a series of examples[4] he came to the conclusion that investigations of selectivity and its relation to reactivity should be continued and used possibly to characterise a certain type of reaction or certain mechanism. Curci *et al.*[13] and Di Furia and co-workers,[14] from theoretical and experimental study, have proved that upon considerably increasing substrate nucleophilicity, particularly in the oxidation of organic sulfides and sulfoxides with dioxiranes and peroxides, the selectivity is not diminished which is in violation of the reactivity–selectivity principle.

The study of the applicability of RSP to biologically relevant oxygen atom transfer reactions is of current interest. Recently, RSP has been successfully applied in the oxidation of organic sulfides[15-17] with PhIO catalysed by (salen)M$^{III}$ (M = Cr, Mn, Ru) complexes and organic sulfoxides[18] with PhIO catalysed by (salen)Mn$^{III}$ complexes. Rajagopal and co-workers[19] have studied the applicability of RSP in the oxidation of organic sulfides with oxo(salen)iron complexes. Recently, we have reported the kinetics and mechanism of (salen)Mn$^{III}$ catalysed oxidation of organic sulfides with sodium hypochlorite.[20] Herein we report the applicability and mathematical verification of RSP in the oxidation of aryl methyl sulfides with oxo(salen)manganese(V) complexes **2a–d** generated *in situ* from the corresponding [(salen)Mn$^{III}$]$^+$PF$_6^-$ complexes and NaOCl as represented in Eqn (1).



1 2 (1)

**a** : unsubstituted
**b** : 5,5'-$(OCH_3)_2$
**c** : 5,5'-$Cl_2$
**d** : 5,5'-$(NO_2)_2$

## Experimental

*Materials*

Thioanisole and *para*-substituted thioanisoles were prepared according to the literature procedure[21,22] and were purified by the usual methods. The purity of the sulfides was checked by $^1$H NMR spectra and HPLC analyses. Sodium hypochlorite was estimated by an iodometric method. Acetonitrile (GR, E.Merck) was first refluxed over $P_2O_5$ for 5 h and then distilled. Doubly distilled water was used throughout the experiment.

The [(salen)Mn$^{III}$]$^+$PF$_6^-$ complexes **1a–d** were synthesised according to the reported procedure.[18,23] The results of IR and UV-visible spectral studies of these complexes were found to be identical with literature data.[18,23] The oxo(salen)manganese(V) complexes **2a–d** were obtained by mixing equimolar quantities of complex and sodium hypochlorite. As oxomanganese(V) complexes undergo auto-decomposition, the solutions were prepared freshly for each kinetic run.

*Kinetic measurements*

The kinetic measurements were carried out in 90% acetonitrile–10% water(v/v) at 20 ± 0.1°C under pseudo first-order conditions ([sulfide]>[oxo complex]) using a Perkin-Elmer UV-visible spectrophotometer (Lambda 3B) fitted with thermostated cell compartments. 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 progress of the reaction was monitored by following the decay of oxo complex at 680 nm.

The rate constants were obtained from the slopes of linear plots of $\log(A_t–A_\infty)$ versus time, where $A_t$ is the absorbance at time 't' and $A_\infty$ is the experimentally determined infinity point. The values of $k_1$ were obtained from $k_1 = k_{1(obs)}–k_{1(dec)}$ where $k_{1(dec)}$ represents the first-order rate constants for the auto-decomposition of oxo complex and $k_{1(obs)}$ represents the pseudo first-order rate constants for the decay of oxo complex in the presence of sulfides. The second-order rate constants were obtained from $k_2 = k_1/[\text{sulfide}]$.

*Product analysis*

The reaction mixture from an actual kinetic run was subjected to vacuum evaporation and the residue was then extracted with chloroform. The extract was dried over anhydrous $Na_2SO_4$ and the solvent evaporated. The product was dissolved in methylene chloride and the gas chromatographic analyses of the samples showed that sulfoxide was the sole product. The retention times obtained for the sulfides were around 2.4 min. The retention times for methyl phenyl sulfoxide, *p*-chlorophenyl methyl sulfoxide and *p*-methoxyphenyl methyl sulfoxide were 5.7, 5.3 and 6.5 min respectively. A similar gas chromatographic analysis was carried out for the entire set of substrates used in the present study. The yield of sulfoxide, ranging between 70–85%, depended on the sulfide and oxomanganese(V) complex employed.

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* Correspondence.

*Stoichiometry*

The reaction studied under the experimental conditions ([**2a**] = 0.0026M; [PhSMe] = 0.20M) gave sulfoxide in *ca* 72% yield and (salen)Mn$^{III}$ complex in *ca*. 95% yield with a negligible amount of sulfone. Accordingly, the stoichiometry for the oxidation of sulfides with oxo complexes can be represented by Eqn (2).

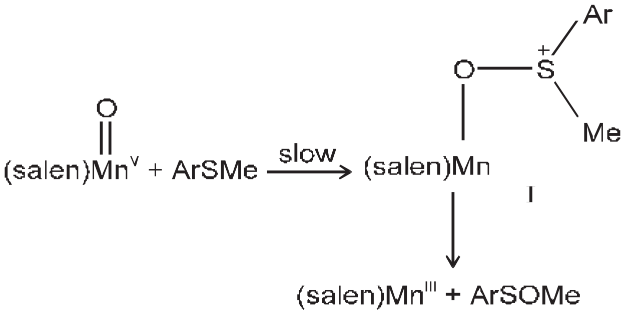
$$O{=}Mn^{V}(salen)^{+} + PhSMe \longrightarrow Mn^{III}(salen)^{+} + PhSOMe \quad (2)$$

*Results and discussion*

The constant values of first-order rate constants($k_1$) at different initial concentrations of **2a** and the concordant values of second-order rate constants($k_2$) for different initial concentrations of methyl phenyl sulfide (MPS) reported in Table 1 reveal that the reaction is overall second-order, first-order each in the oxidant and the sulfide. A mechanism involving the electrophilic attack of the oxidant on the sulfide sulfur has been proposed.[20] The proposed mechanism (Scheme 1) envisages the formation of intermediate I in the slow step, which then decomposes to give (salen)Mn$^{III}$ and sulfoxide as the products.

The second-order rate constants for the reactions of various *para*-substituted phenyl methyl sulfides with each of the oxo(salen) manganese(V) complexes **2a–d** are collected in Table 2. Electron-releasing substituents in the sulfide and electron-withdrawing substituents in the oxo(salen)manganese(V) complex enhance the rate of oxidation.

The kinetic data for the reactions of various thioanisoles with a given oxo(salen)manganese(V) complex and various oxo(salen)manganese(V) complexes with a given sulfide have been correlated with Hammett substituent constants. The last row of Table 2 contains ρ values for substituent variation in sulfide for each oxo(salen)manganese(V) complex and the last column shows reaction constants for substituent variation in oxo(salen)manganese(V) complex for each sulfide. The ρ values show that there is a significant variation of reaction constants (selectivity) when we vary the nature of substituent either in the oxo(salen)manganese(V) complex or in the sulfide. It is apparent that as the reactivity of either sulfide or oxo(salen)manganese(V) complex decreases, the ρ value increases, *i.e.*, there is an inverse relationship between reactivity and selectivity in both the cases.



**Scheme 1**

*Mathematical verification*

When two reagents (fast F and slow S) and a series of similar substrates ($i$ = 1, 2, 3 . . . $n$) 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 (3).

$$\log k_{Fi} = a + b \log k_{Si} + \varepsilon_i \quad (3)$$

where $k_{Fi}$ and $k_{Si}$ are the second-order rate constants for the reactions of fast and slow reagents (oxo(salen)manganese(V) complexes), respectively, with each sulfide and $\varepsilon_i$ is the error of the log $k_{Fi}$ versus log $k_{Si}$ correlation. Since the difference between the reagents is variable along the series of substrates, the mean difference, Δ, can be calculated using Eqn (4).

$$\Delta = (\sum_i \log k_{FI} - \sum_i \log k_{Si})/N \quad (4)$$

**Table 1** Rate constants for the oxidation of MPS by oxo(salen)manganese(V) complexes **2a–d** in 90% acetonitrile–10% water(v/v) at 20°C[a]

| $10^2$[MPS]$_o$ /M | $10^3$[**2**]$_o$ /M | $10^4 k_{1(obs)}$[b] /s-1 | $10^4 k_{1(dec)}$[c] /s-1 | $10^4 k_1$[d] /s$^{-1}$ | $10^3 k_2$[e] /M$^{-1}$s$^{-1}$ |
|---|---|---|---|---|---|
| | **2a** | | | | |
| 10.0 | 1.00 | 10.0 ± 0.2 | 5.44 ± 0.09 | 4.56 ± 0.11 | 4.56 ± 0.11 |
| 10.0 | 1.60 | 9.97 ± 0.17 | 5.72 ± 0.16 | 4.25 ± 0.01 | 4.25 ± 0.01 |
| 10.0 | 2.00 | 9.58 ± 0.21 | 5.24 ± 0.09 | 4.34 ± 0.12 | 4.34 ± 0.12 |
| 10.0 | 2.60 | 9.97 ± 0.19 | 5.52 ± 0.03 | 4.45 ± 0.16 | 4.45 ± 0.16 |
| 10.0 | 3.00 | 10.2 ± 0.2 | 5.79 ± 0.16 | 4.41 ± 0.04 | 4.41 ± 0.04 |
| 10.0 | 3.60 | 10.3 ± 0.1 | 5.99 ± 0.05 | 4.31 ± 0.05 | 4.31 ± 0.05 |
| 5.0 | 2.60 | 7.75 ± 0.15 | 5.52 ± 0.03 | 2.23 ± 0.12 | 4.46 ± 0.24 |
| 15.0 | 2.60 | 11.8 ± 0.2 | 5.52 ± 0.03 | 6.28 ± 0.17 | 4.19 ± 0.11 |
| 20.0 | 2.60 | 14.1 ± 0.3 | 5.52 ± 0.03 | 8.58 ± 0.27 | 4.29 ± 0.14 |
| 40.0 | 2.60 | 22.0 ± 0.6 | 5.52 ± 0.03 | 16.5 ± 0.6 | 4.13 ± 0.15 |
| 50.0 | 2.60 | 26.8 ± 0.6 | 5.52 ± 0.03 | 21.3 ± 0.6 | 4.26 ± 0.12 |
| 100.0 | 2.60 | 51.3 ± 1.4 | 5.52 ± 0.03 | 45.8 ± 1.4 | 4.58 ± 0.14 |
| | **2b** | | | | |
| 10.0 | 2.60 | 7.61 ± 0.10 | 4.68 ± 0.04 | 2.93 ± 0.06 | 2.93 ± 0.06 |
| 20.0 | 2.60 | 10.5 ± 0.3 | 4.68 ± 0.04 | 5.82 ± 0.26 | 2.91 ± 0.13 |
| 40.0 | 2.60 | 16.2 ± 0.5 | 4.68 ± 0.04 | 11.5 ± 0.5 | 2.88 ± 0.13 |
| 50.0 | 2.60 | 19.4 ± 0.6 | 4.68 ± 0.04 | 14.7 ± 0.6 | 2.94 ± 0.12 |
| 100.0 | 2.60 | 32.1 ± 1.2 | 4.68 ± 0.04 | 27.4 ± 1.2 | 2.74 ± 0.12 |
| | **2c** | | | | |
| 2.5 | 2.60 | 7.92 ± 0.26 | 5.59 ± 0.07 | 2.33 ± 0.19 | 9.32 ± 0.76 |
| 5.0 | 2.60 | 10.6 ± 0.4 | 5.59 ± 0.07 | 5.01 ± 0.33 | 10.0 ± 0.7 |
| 10.0 | 2.60 | 14.7 ± 0.5 | 5.59 ± 0.07 | 9.11 ± 0.43 | 9.11 ± 0.43 |
| 20.0 | 2.60 | 24.0 ± 0.6 | 5.59 ± 0.07 | 18.4 ± 0.5 | 9.20 ± 0.25 |
| 25.0 | 2.60 | 29.0 ± 0.8 | 5.59 ± 0.07 | 23.4 ± 0.7 | 9.36 ± 0.28 |
| | **2d** | | | | |
| 2.5 | 2.60 | 12.8 ± 0.4 | 5.97 ± 0.04 | 6.83 ± 0.36 | 27.3 ± 1.4 |
| 5.0 | 2.60 | 20.3 ± 0.3 | 5.97 ± 0.04 | 14.3 ± 0.3 | 28.6 ± 0.6 |
| 10.0 | 2.60 | 33.6 ± 0.7 | 5.97 ± 0.04 | 27.6 ± 0.7 | 27.6 ± 0.7 |
| 20.0 | 2.60 | 59.6 ± 2.2 | 5.97 ± 0.04 | 53.6 ± 2.2 | 26.8 ± 1.1 |
| 25.0 | 2.60 | 73.0 ± 2.9 | 5.97 ± 0.04 | 67.0 ± 2.9 | 26.8 ± 1.2 |

[a]As determined by a spectrophotometric technique following the disappearance of oxomanganese(V) at 680 nm; the error quoted in $k$ value is the 95% confidence limit of Student's $t$-test.[24] [b]Estimated from pseudo first-order plots over 40% 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 $k_1$/[sulfide]$_0$.

**Table 2** Second-order rate constants and ρ values for the reactions of *p*-$XC_6H_4SMe$ with **2a–d** in 90% acetonitrile–10% water(v/v) at 20°C[a,b]

| | Oxo(salen)manganese(V) complex $10^3k_2/M^{-1}s^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| X | **2b** | **2a** | **2c** | **2d** | $\rho^d$ | (*r*) |
| OMe | 14.3 ± 0.6 | 16.5 ± 0.7 | 23.1 ± 0.8 | 35.3 ± 1.3 | 0.193 ± 0.018 | (0.991) |
| Me | 6.05 ± 0.15 | 10.2 ± 0.4 | 14.6 ± 0.5 | 28.8 ± 1.3 | 0.317 ± 0.025 | (0.994) |
| H | 2.91 ± 0.13 | 4.29 ± 0 14 | 9.20 ± 0.25 | 26.8 ± 1.1 | 0.476 ± 0.038 | (0.994) |
| F | 2.19 ± 0.04 | 3.64 ± 0.19 | 7.90 ± 0.25 | 21.4 ± 0.6 | 0.480 ± 0.041 | (0.993) |
| Cl | 1.17 ± 0.04 | 2.03 ± 0.06 | 4.31 ± 0.22 | 12.8 ± 0.4 | 0.502 ± 0.031 | (0.996) |
| Br | 0.98 ± 0.04 | 1.66 ± 0.09 | 3.91 ± 0.22 | 11.1 ± 0.3 | 0.515 ± 0.046 | (0.992) |
| COOH[c] | 0.48 ± 0.04 | 0.76 ± 0.08 | 2.79 ± 0.18 | 7.03 ± 0.36 | 0.581 ± 0.103 | (0.970) |
| COMe | 0.26 ± 0.04 | 0.55 ± 0.08 | 1.71 ± 0.08 | 4.17 ± 0.23 | 0.583 ± 0.094 | (0.975) |
| $NO_2$ | 0.09 ± 0.02 | 0.18 ± 0.04 | 0.53 ± 0.04 | 1.84 ± 0.09 | 0.634 ± 0.062 | (0.991) |
| $\rho^e$ | –2.02 ± 0.08 | –1.85 ± 0.04 | –1.47 ± 0.08 | –1.25 ± 0.10 | | |
| (r) | (0.995) | (0.998) | (0.991) | (0.978) | | |

[a]The errors quoted in $k_2$ is the 95% confidence limit of Student's *t*–test.[24] [b]General conditions: $[\mathbf{2}]_o$ = 0.0026 M; $[\text{sulfide}]_o$ = 0.20 M. [c]$[\text{sulfide}]_o$ = 0.10 M. [d]The values were obtained by correlating log $k_2$ with $2\sigma_p$ values[25] for the reaction of various oxo(salen)manganese(V) complexes with a given sulfide. [e]The values were obtained by correlating log $k_2$ with $\sigma_p$ values[25] for the reaction of various sulfide with a given oxo(salen)manganese(V) complex.

**Table 3** Results of correlation between log $k_{Fi}$ and log $k_{Si}$ for aryl methyl sulfides

| | Oxo(salen)manganese(V) complexes (F&S) | | | | | |
|---|---|---|---|---|---|---|
| Results | **2a** and **2b** | **2c** and **2b** | **2c** and **2a** | **2d** and **2b** | **2d** and **2a** | **2d** and **2c** |
| *r* | 0.997 | 0.992 | 0.991 | 0.973 | 0.974 | 0.986 |
| *b* | 0.906 ± 0.025 | 0.725 ± 0.036 | 0.798 ± 0.040 | 0.612 ± 0.055 | 0.675 ± 0.059 | 0.849 ± 0.028 |
| Δ | 0.221 | 0.573 | 0.352 | 0.935 | 0.714 | 0.362 |

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

With the rate data available in Table 2, log $k_{Fi}$ values were plotted against log $k_{Si}$ values according to Eqn (3) to find slope b and the values of Δ were calculated using Eqn (4) for all the six possible combinations of one fast and one slow reagent (among the four oxo(salen)manganese(V) complexes) with a series of similar substrates (nine aryl methyl sulfides) (Fig. 1). The results summarised in Table 3 show a valid RSP in all the 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 $k_{Fi}$ versus log $k_{Si}$ 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. Figure 1 reveals that the correlations involving nitro-substituted oxo complex **2d** (lines d,e and f) are consistent with a magic point, $y_0$, whereas the correlations involving other oxo complexes (lines a, b & c) do not exhibit a distinct magic point. The magic point, $y_o$ is situated on the side of high reactivity as expected for a valid RSP as observed in the oxidation of sulfides,[15] sulfoxides,[18] aliphatic alcohols[26] and substituted benzyl alcohols[27] with PhIO catalysed by (salen)$Mn^{III}$ complexes and in the oxidation of sulfides with oxo(salen)chromium(V) complexes,[16] oxo(salen)ruthenium(V) complexes[17] and oxo(salen)iron complexes.[19]

The second-order rate constants for the oxidation of *para*-substituted phenyl methyl sulfides by **2a** at four different temperatures have been reported.[20] The Hammett ρ values at 293, 298, 303 and 313 K are –1.85, –1.80, –1.76 and –1.72, respectively, pointing to a decrease in selectivity with an increase in temperature *i.e.*, with an increase in the reactivity. Thus, the present redox system obeys the RSP.[4,16]

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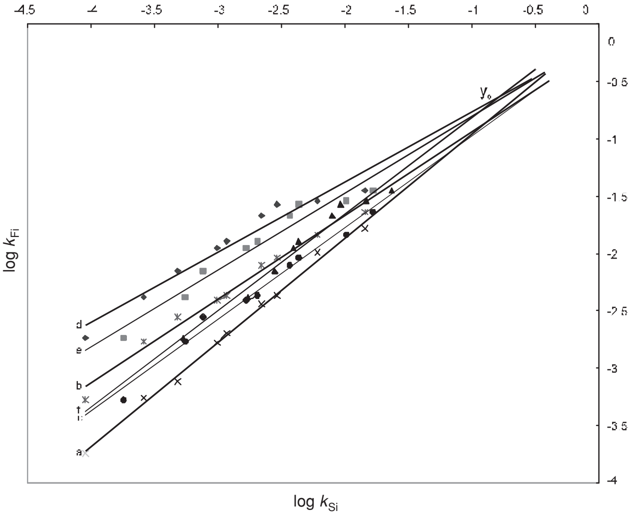

**Fig 1** Log $k_{Fi}$ versus log $k_{Si}$ plots for the reactions of aryl methyl sulfides with (a) **2a** and **2b**, (b) **2c** and **2b**, (c) **2c** and **2a**, (d) **2b** and **2b**, (e) **2d** and **2a**, and (f) **2d** and **2c**.

## 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. R.V. Sendega, R.V. Vizgert and M.K. Mikhalevich, *Reakts. Sposobnost Org. Soedin. (Tartu),* 1970, **7,** 512.
6. C. Srinivasan, P. Kuthalingam and N. Arumugam, *Can. J. Chem.,* 1978, **56,** 3043; *J. Chem. Soc., Perkin Trans. 2,* 1980, 170.
7. I. Lee, H.J. Koh, Y.S. Park and H.W. Lee, *J. Chem. Soc., Perkin Trans.2,*1993, 1575.
8. 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.
9. L.M. Stock and H.C. Brown, *Adv. Phys. Org. Chem.,* 1963, **1,** 35.
10. E. Buncel and C.J. Chanqui, *J. Org. Chem.,* 1980, **45,** 2825; M.E. Arnett and K.E. Molter, *Acc. Chem. Res.,* 1985, **18,** 339.

11. D.A. Jencks and W.P. Jencks, *J. Am. Chem. Soc.,* 1977, **99**, 7984; W.P. Jencks, *Chem. Rev.,* 1985, **85,** 511.
12. E. Buncel and H. Wilson, *J. Chem. Ed.,* 1987, **64,** 476.
13. R. Curci, A. Dinoi and M.F. Rubino, *Pure and Appl. Chem.,* 1995, **67,** 811.
14. M. Bonchio, S. Campestrini, V. Conte, F. Di Furia and S. Moro, *Tetrahedron,* 1995, **51,** 12363.
15. A. Chellamani, N.M.I. Alhaji and S. Rajagopal, *J. Chem. Soc., Perkin Trans. 2,* 1997, 299; A. Chellamani and N.M.I. Alhaji, *Indian J. Chem.,* 1999, **38A,** 888.
16. R. Sevvel, S. Rajagopal, C. Srinivasan, N.M.I. Alhaji and A., Chellamani, *J. Org. Chem.,* 2000, **65,** 334.
17. P. Kulanthaipandi, Ph.D Thesis, Manonmaniam Sundaranar University, 1999.
18. A. Chellamani, P. Kulanthaipandi and S. Rajagopal, *J. Org. Chem.,* 1999, **64,** 2232.
19. V.K. Sivasubramanian, M. Ganesan, S. Rajagopal and R. Ramaraj, *J. Org. Chem.,* 2002**, 67,** 1506.
20. A. Chellamani and S. Harikengaram, *J. Phys. Org. Chem.,* 2003, **16,** 589.
21. C. Srinivasan, A. Chellamani and S. Rajagopal, *J. Org. Chem.,* 1985, **50,** 1201.
22. A. Chellamani, N.M.I. Alhaji, S. Rajagopal, R. Sevvel and C. Srinivasan, *Tetrahedron,* 1995, **51,** 12677.
23. K. Srinivasan, P. Michaud and J.K. Kochi, *J. Am. Chem. Soc.,* 1986, **108,** 2309.
24. C. Srinivasan, S. Rajagopal and A. Chellamani *J. Chem. Soc. Perkin Trans. 2,* 1990, 1839.
25. J. Shorter, *Correlation Analysis in Organic Chemistry,* Clarendon Press, Oxford, 1973, p.14.
26. V. Bansal, P.K. Sharma and K.K. Banerji, *Indian J. Chem.,* 2000, **39A,** 654.
27. V. Kumbhat, P.K. Sharma and K.K. Banerji, *J. Chem. Res.*(S) 2001, 179; (M) 562.