J. Braz. Chem. Soc., Vol. 19, No. 8, 1484-1489, 2008.
Printed in Brazil - ©2008 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Oxidation of Mono-Phenols to *para*-Benzoquinones: a Comparative Study

Marciana P. Uliana, Ygor W. Vieira, Maria Carolina Donatoni, Arlene G. Corrêa, Ursula Brocksom and Timothy J. Brocksom*

Departamento de Química, Universidade Federal de São Carlos, 13565-905 São Carlos-SP, Brazil

A oxidação de mono-fenóis à *para*-benzoquinonas é assunto de interesse contínuo devido à existência de inúmeros produtos naturais contendo esta unidade estrutural. As *para*-benzoquinonas possuem reatividade química importante como agentes oxidantes e como dienófilos na reação de Diels-Alder. Usualmente nós preparamos as *para*-benzoquinonas pela reação de oxidação dos respectivos mono-fenóis com oxigênio molecular e catalisada por [Co^{II}(salen)]. Porém, foi necessário estudar estas oxidações utilizando-se outros oxidantes. Nós apresentamos aqui nossos resultados sobre esta importante reação de oxidação com uma variedade de oxidantes, utilizando onze mono-fenóis como substratos. Os oxidantes utilizados foram cobalto, níquel, cobre e vanádio derivados com alguns ligantes do tipo salen. Também foram estudados peróxido de hidrogênio, OXONE®, dimetil dioxirano e ácido iodoxibenzóico.

The oxidation of mono-phenols to *para*-benzoquinones is of continuing interest due to the existence of numerous natural products containing this structural unit. The chemical reactivity of *para*-benzoquinones is also noteworthy, as oxidants and dienophiles in the Diels-Alder reaction. We have used for quite some time now, molecular oxygen and catalysis with [Co^{II}(salen)] as the oxidation procedure, but felt the need for other oxidants and conditions to be of use with different phenol substrates. We now present our results on this important oxidation with a variety of oxidants, using eleven mono-phenols as substrates. The oxidants tested are cobalt, nickel, copper and vanadyl metals, with a selection of different salen type ligands. Completing this study we also investigated the use of hydrogen peroxide, OXONE®, dimethyl dioxirane and iodoxybenzoic acid.

Keywords: oxidation, alkyl-substituted phenols, *para*-benzoquinones

Introduction

Natural products frequently occur containing the *para*-benzoquinone sub-structural unit within the global structure, as can be exemplified by vitamins K_1 and K_2, co-enzyme Q (ubiquinone),[1] and in many terpenes and alkaloids.[2] These natural products[3-13] are associated with important biological properties, such as cardiovascular, anti-tumour, antibacterial, anti-germination and anti-protozoan among others. There is no doubt that the *para*-benzoquinone nucleus is an important charge transfer receptor and easily undergoes nucleophilic addition reactions.[1] The redox relation with *para*-hydroquinones (*para*-quinols) is of importance in biological activity, and also makes many simple *para*-benzoquinones excellent oxidizing agents.[1] Synthetically, the *para*-benzoquinone structural unit is an excellent dienophile for the Diels-Alder reaction, among other relevant reactions.[1]

*e-mail: brocksom@terra.com.br

The usual and obvious manner to prepare *para*-benzoquinones[1,14,15] is from the corresponding *para*-hydroquinones, which is however rather limited due to the lack of a wide range of commercially or synthetically available substrates. As a second choice, the simple mono-phenol is an ideal substrate due to the ready availability of an extremely wide range of such compounds.

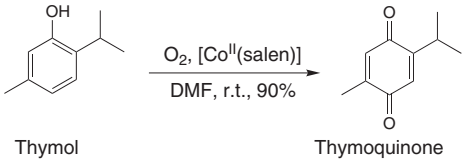
A further point of interest is the large price differential between mono-phenols and the corresponding *para*-benzoquinones, being tens to over a hundred times more expensive when available.[16] All this leads to a continuing interest in methodologies for the oxidation of mono-phenols to *para*-benzoquinones, with an acceptance of varied substitutions on the phenol ring. Historically, this oxidation has required reagents such as Fremy's salt,[17] heavy metal oxidants in large molar excess,[18] or chemical modification of the mono-phenol to introduce an amino group in the *para*-position.[19] However these methods suffer from low yields, inconvenient reagents or multi-step sequences,

and are not applicable to a wide range of substrates. Furthermore, the methodologies are not always susceptible to execution on multi-gram scales.

More recently new oxidants have been introduced, and we have routinely used molecular oxygen in the presence of [Co^{II}(salen)] (or Salcomine) as catalyst, in DMF/H_2O.[20] The catalyst is added in three portions over 12 h, and for certain substrates such as Thymol is an excellent choice (Scheme 1). This result is based upon a fairly extensive study of the [Co^{II}(salen)] catalyst addition, where a certain deactivation is observed with time. Generally the yields fall quite substantially with addition in one portion, or the use of lower loadings of catalyst. As a general rule we use between 4% and 6% mol equivalents in three portions for a total catalyst loading of 12% to 18% mol.

In this paper we would like to present our results of a much more extensive study using eleven different phenol substrates, and varying the metal and ligand with respect to [Co^{II}(salen)], and also the other oxidants hydrogen peroxide, OXONE®, dimethyldioxirane (DMD) and iodoxybenzoic acid (IBX).

The mechanism of this reaction is well accepted[21] as involving one electron oxidation of the phenolate anion to generate the phenoxy radical which then reacts with molecular oxygen to form the *para*-peroxycyclohexadienone. Finally, loss of water produces the *para*-benzoquinone. Competitive reaction of the phenoxy radical with molecular oxygen at the ortho position would lead to the *ortho*-benzoquinone. The usual side reactions also involve the phenoxy radical, and ortho-para and para-para carbon-carbon coupling leads to the bis-quinone-methides, the bis-phenol, and eventually to polymeric materials (Scheme 2; to simplify the Scheme we have omitted ortho-ortho and ortho-para couplings).

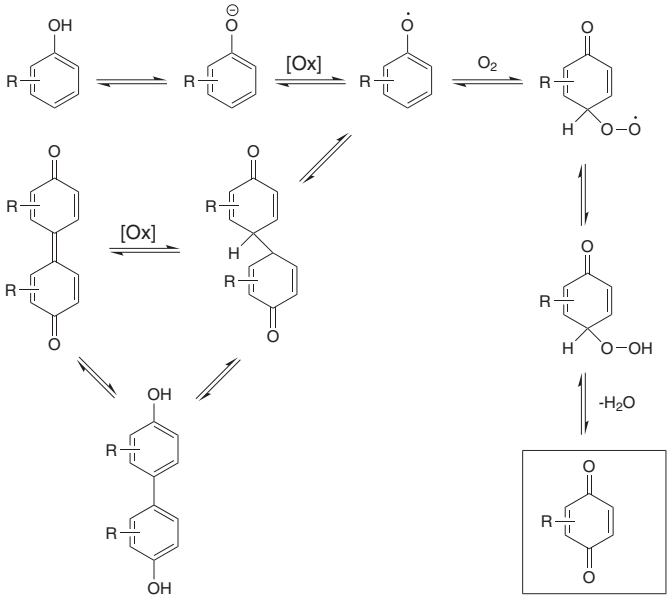


Scheme 1. Thymol oxidation to thymoquinone.

However some of our mono-phenol substrates gave sluggish reactions and lower yields, contamination with the starting mono-phenol and thus separation problems, and difficulties in scale-up, which has led us to study other oxidants.

We have examined the literature, and Table 1 provides some detailed information on published phenol substrates in oxidation with different oxidants. This Table is not meant to be exhaustive but illustrative of the wide variety of oxidants that have been evaluated. The mono-phenol substrates and *para*-benzoquinones products are shown in Figures 1 and 2 respectively.

Table 1 shows some interesting results with the varied oxidants, which are expensive, toxic, explosive or simply inconvenient, or used in large excess. This led us to the present study with some newer oxidants, which were chosen on the basis of availability (including price) or ease of preparation, easy reaction conditions, diminished toxicity problems, and use in more acceptable quantities. These oxidants have been compared with our original system of [Co^{II}(salen)] and variations on this by exchanging the metal and or the ligand.



Scheme 2. The accepted mechanism of oxidation of mono-phenols.

Table 1. Oxidation of mono-phenols to *para*-benzoquinones, as found in the literature

Entry	Phenol	*p*-benzoquinone	Reaction conditions	Yield / (%)	Ref.
1	**1**	**12**	H_2O_2 83%, MTO*, AcOH, 40 ºC, 4 h	31	22
			KO_2, toluene, r.t. 48 h	NR	23
			$[(bpy)_2(py)Ru^{IV}=O]^{2+}$, CH_3CN	88	24
2	**2**	**13**	H_2O_2 83%, MTO*, AcOH, 40 ºC, 4 h	42	22
			$[(bpy)_2(py)Ru^{IV}=O]^{2+}$, CH_3CN	68	24
			H_2O_2 60%, phosphomolybdic acid, AcOH, 30 ºC, 5 h	13	25
3	**3**	**13**	H_2O_2 83%, MTO*, AcOH, 40 ºC, 2 h	24	22
			H_2O_2 60%, phosphomolybdic acid, AcOH, 30 ºC, 5 h	39	25
			H_2O_2 30%, PVP**-25%/MTO*, EtOH, 30 ºC	92	26
4	**4**	**14**	$[(bpy)_2(py)Ru^{IV}=O]^{2+}$, CH_3CN	62	24
5	**5**	**15**	H_2O_2 60%, phosphomolybdic acid, AcOH, 30 ºC, 5 h	25	25
			H_2O_2 30%, PVP**-2%/MTO*, EtOH 30 ºC	85	26
			$PhSeO_2H$, CH_2Cl_2, 1 h, reflux	40	27
			$NaBO_3.4H_2O$/ wet montmorillonite K10	65	28
			H_2O_2 60%, Br_2, H_2SO_4, MeOH, reflux, 20 min	86	29
			O_2, $[Co(bpb)H_2O]$, CH_3CN, 2 h	94	30
6	**6**	**16**	H_2O_2 60%, phosphomolybdic acid, AcOH, 30 ºC, 5 h	67	25
			H_2O_2, $\{(Ce_2L)(Me_2SO)_5\}.2Me_2SO_4$, CH_3CN	38	31
			$HOF.CH_3CN$, 1 min	30	32
7	**7**	**15**	H_2O_2 83%, MTO*, AcOH, 40 ºC, 2 h	43	22
			$[(bpy)_2(py)Ru^{IV}=O]^{2+}$, CH_3CN	86	24
			H_2O_2 60%, phosphomolybdic acid, AcOH, 30 ºC, 5 h	63	25
8	**8**	**17**	H_2O_2 83%, MTO*, AcOH, 40 ºC, 2 h	4	22
			H_2O_2 60%, phosphomolybdic acid, AcOH, 30 ºC, 5 h	64	25
			$PhSeO_2H$, CH_2Cl_2, 2 h, r.t.	75	27
			$HOF.CH_3CN$, 1 min	30	32
9	**9**	**18**	$PhSeO_2H$, CH_2Cl_2, 20 h, r.t.	11	27
			H_2O_2 60%, Br_2, H_2SO_4, MeOH, reflux, 20 min	97	29
			O_2, $[Co(bpb)H_2O]$, CH_3CN, 2 h	96	30
			O_2, Co(saln-Medpt), CH_3CN, 1 h	100	33
			H_2O_2 (6eq), CH_3ReO_3, $[bmim]BF_4$, 60 ºC, 8h	98	34
10	**10**	**19**	$PhSeO_2H$, CH_2Cl_2, 18 h, r.t.	36	27
			$NaBO_3.4H_2O$/ wet montmorillonite K10	63	28
			O_2, Co(saln-medpt), CH_3CN, 0.5 h	100	33
			H_2O_2 (6eq), CH_3ReO_3, $[bmim]BF_4$, 60 ºC, 8 h	98	34
			Bis(trifluoroacetoxy) iodobenzene, CH_3CN, 0 ºC 2 h	73	35
11	**11**	**20**	$(PhSeO)_2O$, reflux, 3 h	73	36
			t-BuOOH, MeOH	65	37

MTO* methyl rhenium trioxide; PVP** poly(4-vinylpyridine).

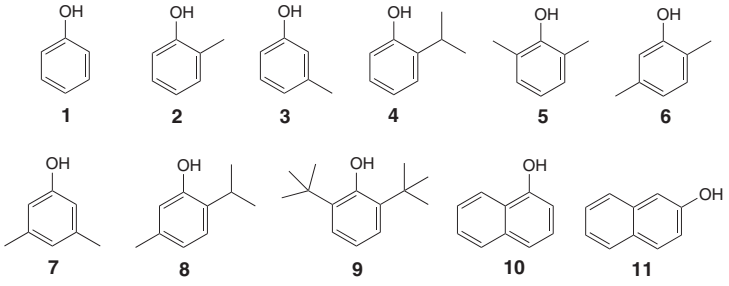


Figure 1. The substrate phenols.

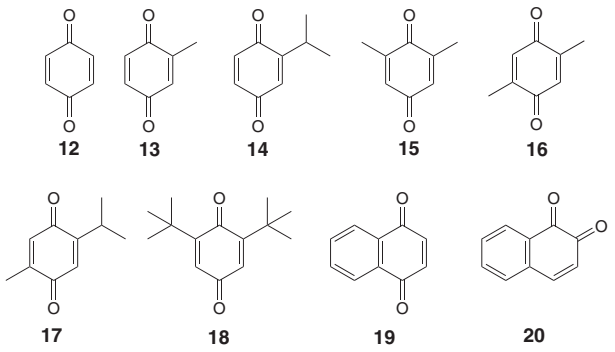


Figure 2. The product quinones.

Results and Discussion

Our choice of phenol substrates (Figure 1) includes obviously phenol (**1**), three mono-alkyl-substituted phenols (**2**)-(**4**), five di-alkyl-substituted phenols (**5**)-(**9**), and α-(**10**) and β-naphthol (**11**), giving a good coverage of possible substitution patterns. The possible *para*-benzoquinone products, (**12**) to (**20**), are shown in Figure 2. The study started with the standard O_2 and [Co^{II}(salen)] experiments, followed by exchange of cobalt for nickel, copper and vanadium. The second exchange involves the ligand salen for other readily accessible ligands of the same type. Figure 3 shows our selection of metal salen type oxidants.

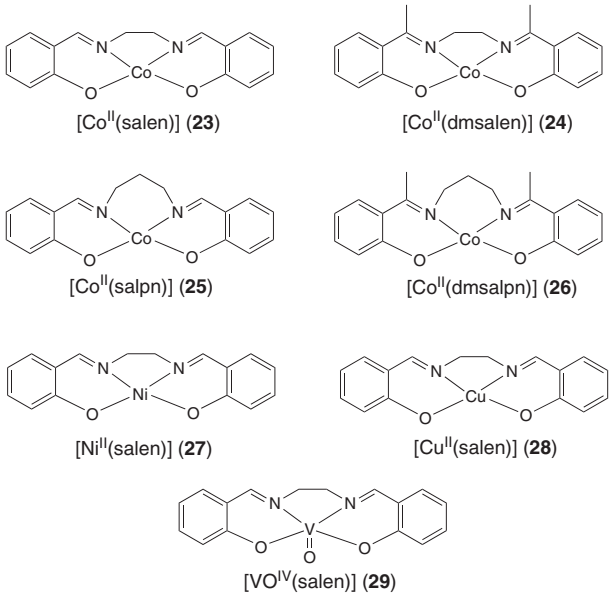


Figure 3. The metal-ligand catalysts.

Table 2 shows our comparative study of the oxidation of the phenols (**1**) to (**11**) against the various metal-ligand catalysts. The *para*-benzoquinone products are all known compounds, and identification was performed by comparison of IR and NMR spectral data, as well as melting points determinations. The first conclusion is that cobalt is essential as the other metals (Ni, Cu and V) do not show any catalytic activity. The second conclusion is that the ligand salen is more efficient than the others ligands, and thus serendipity once again had led to the use of the commercially available complex. The substrates show structural variations on oxidation, and the more highly substituted phenols are more effective substrates.

Table 2. Mono-phenol oxidation with metal salen type complexes; numbers are isolated yields, and NR signifies no reaction

Entry	phenol	**23**	**24**	**25**	**26**
1	**1**	30	<5	NR	NR
2	**2**	54	10	4	NR
3	**3**	34	11	3	NR
4	**4**	40	15	<5	NR
5	**5**	95	25	7	NR
6	**6**	90	23	3	NR
7	**7**	23	9	5	NR
8	**8**	93	32	16	4
9	**9**	97	94	89	22
10	**10**	88	32	30	2
11	**11**	NR	NR	NR	NR

These results suggested a study of other oxidants for the less substituted phenols. With this in mind we looked for simple and readily available oxidants, used in easy reaction conditions, and amenable to green chemistry requirements. The first oxidant which comes to mind is obviously hydrogen peroxide, followed by potassium peroxymonosulphate (OXONE®), and then dimethyldioxirane (DMD) and 2-iodoxybenzoic acid (IBX). Oxone is a very cheap oxidant, and furthermore is used in the simple preparations of DMD and IBX. These latter two oxidants were planned to be tested in the absence and the presence of molecular oxygen, in accordance with the proposed mechanism. The following Table shows our results.

Once again (Table 3), the di-substituted phenols are more reactive, while the other phenols were not affected by OXONE® and DMD. The best results were obtained in the absence of molecular oxygen.

The oxidants H_2O_2 (30%) in the presence of molecular bromine, and IBX are demonstrated to be totally ineffective in the oxidation of all the eleven phenols. It is important to recognize that the statement of the lack of reactivity means recovery of the starting phenols. In the case of 30% H_2O_2 with bromine, the substrate β-naphthol does react but the product is 1-bromo-2-naphthol.[38]

In conclusion, we have shown that several different oxidants, easily and cheaply available, can oxidize mono-

Table 3. Comparison of oxidations of phenols **1**-**11** with OXONE and DMD in the presence and absence of molecular oxigen

			OXONE		DMD	
Entry	Phenols	Quinones	no added O_2	with O_2	no added O_2	with O_2
1	**1**	**12**	NR	NR	NR	NR
2	**2**	**13**	NR	NR	NR	NR
3	**3**	**13**	NR	NR	NR	NR
4	**4**	**14**	< 5	< 5	NR	NR
5	**5**	**15**	14	10	16	10
6	**6**	**16**	33	14	23	19
7	**7**	**15**	32	20	22	19
8	**8**	**17**	41	<5	22	11
9	**9**	**18**	NR	NR	NR	NR
10	**10**	**19**	NR	NR	NR	NR
11	**11**	**20**	traces	traces	NR	NR

phenols in reasonable to excellent yields and in a highly regioselective manner. In none of the oxidations under study, have we observed the formation of the isomeric *ortho*-benzoquinone products, nor do we observe quinine-methides or di-phenolic products that could be expected from the proposed mechanism (Scheme 2).

Experimental

General

^{1}H and ^{13}C NMR spectra were obtained on a Bruker DRX-400 spectrometer at 400 and 100 MHz, and on a Bruker ARX-200 spectrometer at 200 and 50 MHz respectively, with $CDCl_3$ as solvent. Chemical shifts are in ppm downfield from a tetramethylsilane internal standard. Infrared spectra were recorded on Bomen Michelson model 102 FTIR or Hartman & Braun MB, and the most intense or representative bands are reported (in cm^{-1}). Melting points were determined on a Micro Química model APF 301 apparatus and are uncorrected. Gas liquid chromatographic analyses were performed on a Shimadzu GC-17A, equipped with a DB-1 capillary column (0.25 mm × 30 m) and using nitrogen as carrier gas. Solvents and reagents were used directly from the manufacturer, or purified when required by standard procedures. The eleven phenols and salen, [Co^{II}(salen)] and [Ni^{II}(salen)] are commercially available products (Aldrich) and used as obtained. The other ligands, salpn, dmsalen and dmsalpn, were prepared by condensation of the appropriate diamine with salicylaldehyde, in dry methanol.[39-41] The other complexes, [Co^{II}(dmsalen)], [Co^{II}(salpn)], [Co^{II}(dmsalpn)], [Cu^{II}(salen)], and [VO^{IV}(salen)], were prepared as described in the cited references. Dimethyldioxirane[42] and iodoxybenzoic acid[43] were prepared according to published procedures.

General procedure for the metal complex catalyzed oxidations

The phenol (1.0 mmol), was dissolved in DMF (5 mL), and oxygen was bubbled into the reaction mixture for a few minutes, and then an oxygen atmosphere was maintained with a balloon. The catalyst (6% mol) was added, and stirred at room temperature for 3 h. Further catalyst (6% mol) was added and the reaction mixture stirred for 3 h at room temperature. The process was repeated once more, for a total addition of 18% mol catalyst, and a total reaction time of 24 h. Ether (20 mL) was added and the black mixture washed with 0.1 mol L^{-1} HCl (2 × 10 mL), water and brine. The ethereal solution was dried over anhydrous $MgSO_4$ and the solvent evaporated: the residue was purified by flash column chromatography using as eluent a mixture of 9:1 hexane:ethyl acetate to give the product.

General procedure for the OXONE® oxidations

An aqueous Na_2.EDTA solution (20 mL, 4×10^{-4} mol L^{-1}) was added to a solution of the phenol (0.5 mmol) in CH_3CN (30 mL), at room temperature. To this solution was added a mixture of OXONE® (2.5 mmol) and $NaHCO_3$ (7.75 mmol). After stirring at room temperature for 24 h, the reaction mixture was poured into brine and extracted three times with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated. The pure product was obtained by flash column chromatography using as eluent a mixture of 9:1 hexane:ethyl acetate.

General procedure for the DMD oxidations

The phenol (2 mmol) was dissolved in acetone (4 mL) and distilled water (4 mL), and OXONE® (3 mmol) and $NaHCO_3$ (8 mmol) were added. The mixture was stirred at

room temperature for 24 h, more water added, and extracted with EtOAc, washed with brine and dried over anhydrous $MgSO_4$. The corresponding *para*-benzoquinone was obtained after purification by flash column chromatography using as eluent a mixture of 9:1 hexane:ethyl acetate.

Acknowledgments

The authors thank FAPESP, CNPq and CAPES for financial support and fellowships.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br, as PDF file.

References

1. Streitweiser, A.; Heathcock, C. H.; Kosower, E. M.; *Introduction to Organic Chemistry*, 4th ed.; Macmillan Publishing Company: New York, 1992, p. 1032.
2. Fraga, B. M.; *Nat. Prod. Rep.* **2007**, *24*, 1350; Hanson, J. R.; *Nat. Prod. Rep.* **2007**, *24*, 1332; Blunt, J. W.; Copp, B. R.; Hu, W-P.; Munro, M. H. G.; Northcote, P. T.; Prinsep, M. R.; *Nat. Prod. Rep*. **2008**, *25*, 35.
3. Chan-Bacab, M. J.; Peña-Rodríguez, L. M.; *Nat. Prod. Rep*. **2001**, *18*, 674.
4. Hoet, S.; Opperdoes, F.; Brun, R.; Quetin-Leclercq, J.; *Nat. Prod. Rep.* **2004**, *21*, 353.
5. Antunes, E. M.; Copp, B. R.; Davies-Coleman, M. T.; Samaai, T.; *Nat. Prod. Rep*. **2005**, *22*, 62.
6. Bililign, T.; Griffith, B. R.; Thorson, J. S.; *Nat. Prod. Rep*. **2005**, *22*, 742.
7. Le Sann, C.; *Nat. Prod. Rep*. **2006**, *23*, 357.
8. Hertweck, C.; Luzhetskyy, A.; Rebets, Y.; Bechthold, A.; *Nat. Prod. Rep*. **2007**, *24*, 162.
9. Copp, B. R.; Pearce, A. N.; *Nat. Prod. Rep*. **2007**, *24*, 278.
10. Bulger, P. G.; Bagal, S. K.; Marquez, R.; *Nat. Prod. Rep*. **2008**, *25*, 254.
11. Morris, J. C.; Phillips, A. J.; *Nat. Prod. Rep*. **2008**, *25*, 95.
12. Whiting, D. A.; *Nat. Prod. Rep*. **2001**, *18*, 583.
13. Sperry, J.; Bachu, P.; Brimble, M. A.; *Nat. Prod. Rep*. **2008**, *25*, 376.
14. Owton, W. M.; *J. Chem. Soc., Perkin Trans. 1* **1999**, 2409.
15. Behrman, E. J.; *J. Braz. Chem. Soc*. **2007**, *18*, 1461.
16. Acros Organics; *Catalog of Organic and Fine Chemicals*, Fisher Scientific, 2007/ 2008, Vol. 282, p.1927.
17. Zimmer, H.; Lankin, D. C.; Horgan, S. W.; *Chem. Rev*. **1971**, *71*, 229.
18. Liotta, D.; Arbiser, J.; Short, J. W.; Saindane, M.; *J. Org. Chem.* **1983**, *48*, 2932.
19. Kremers, E.; Wakeman, N.; Hixon, R. M.; *Org. Synth.* **1967**, 511.
20. Dockal, E. R.; Cass, Q. B.; Brocksom, T. J.; Brocksom, U.; Corrêa, A. G.; *Synth. Commun.* **1985**, *15,* 1033.
21. Bozell, J. J.; Hames, B. R.; *J. Org. Chem.* **1995**, *60*, 2398.
22. Adam, W.; Herrmann, W. A.; Lin, J.; Saha-Möller, C. R.; *J. Org. Chem.* **1994**, *59*, 8281.
23. Crank, G.; Makin, M. I. H.; *Tetrahedron Lett*. **1979**, *23*, 2169.
24. Seok, W. K.; Meyer, T. J.; *J. Am. Chem. Soc.* **1988**, *110*, 7358.
25. Shimizu, M.; Orita, H.; Hayakawa, T.; Takehira, K.; *Tetrahedron Lett*. **1989**, *30*, 471.
26. Saladino, R.; Neri, V.; Mincione, E.; Filippone, P.; *Tetrahedron* **2002**, *58*, 8493.
27. Barton, D. H. R.; Finet, J-P.; Thomas, M.; *Tetrahedron* **1988**, *44*, 6397.
28. Hashemi, M. M.; Eftekhari-Sis, B.; Khalili, B.; Karimi-Jaberi, Z.; *J. Braz. Chem. Soc.* **2005**, *16*, 1082.; Behrman, E. J.; *J. Braz. Chem. Soc.* **2007**, *18*, 1461.
29. Minisci, F.; Citterio, A.; Vismara, E.; Fontana, F.; Bernardinis, S. D.; *J. Org. Chem.* **1989**, *54*, 728.
30. Ganeshpure, P. A.; Sudalai, A.; Satish, S.; *Tetrahedron Lett*. **1989**, *30*, 5929.
31. Chawla, H. M.; Hooda, U.; Singh, V.; *J. Chem. Soc., Chem. Commun.* **1994**, 617.
32. Kol, M.; Rozen, S.; *J. Org. Chem.* **1993**, *58*, 1593.
33. Gaudemer, A.; Nguyen-Van-Duong, K.; Shahkarami, N.; Achi, S. S.; Frostin-Rio, M.; Pujol, D.; *Tetrahedron* **1985**, *41,* 4095.
34. Bernini, R.; Mincione, E.; Barontini, M.; Fabrizi, G.; Pasqualetti, M.; Tempesta, S.; *Tetrahedron* **2006**, *62*, 7733.
35. Barret, R.; Daudon, M.; *Tetrahedron Lett.* **1990**, *31*, 4871.
36. Sukumaran, K. B.; Harvey, R. G.; *J. Org. Chem*. **1980**, *45*, 4407.
37. Suresh, S.; Skaria, S.; Ponrathnam, S.; *Synth. Commun*. **1996**, *26*, 2113.
38. Vyas, P. V.; Bhatt, A. K.; Ramachandraiah, G.; Bedekar, A. V.; *Tetrahedron Lett*. **2003**, *44*, 4085.
39. Hariharan, M.; Urbach, F. L.; *Inorg. Chem.* **1969**, *8*, 556.
40. Bencini, A.; Benelli, C.; Caneschi, A.; Carlin, R. L.; Dei, A.; Gatteschi, D.; *J. Am. Chem. Soc.* **1985**, *107,* 8128.
41. Alvarez, H. M.; Andrade, J. L.; Pereira Jr, N.; Muri, E. M. F.; Horn Jr, A.; Barbosa, D. P.; Antunes, O. A. C.; *Catal. Commun.* **2007**, *8,* 1336.
42. Ferraz, H. M. C.; Muzzi, R. M.; Vieira, T. O.; Viertler, H.; *Tetrahedron Lett*. **2000**, *41*, 5021.
43. Frigerio, M.; Santagostino, M.; Sputore, S.; *J. Org. Chem*. **1999**, *64*, 4537.

Received: April 10, 2008
Web Release Date: September 10, 2008

FAPESP helped in meeting the publication costs of this article.