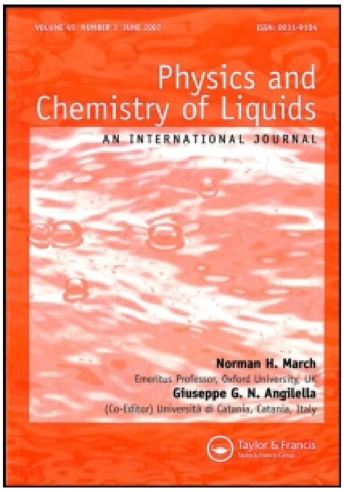

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Studies on the catalysis by lithium perchlorate and lithium trifluoromethanesulfonate of the photo-oxidation of phenols and <i>α</i>-phellandrene in different solvents

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To cite this Article Kinart, Wojciech J. , Kinart, Andrzej and Kozak, Monika(2007) 'Studies on the catalysis by lithium perchlorate and lithium trifluoromethanesulfonate of the photo-oxidation of phenols and <i>α</i>-phellandrene in different solvents', Physics and Chemistry of Liquids, 45: 6, 663 — 673

To link to this Article: DOI: 10.1080/00319100701434338

URL: http://dx.doi.org/10.1080/00319100701434338

Physics and Chemistry of Liquids
Vol. 45, No. 6, December 2007, 663–673

Taylor & Francis
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Studies on the catalysis by lithium perchlorate and lithium trifluoromethanesulfonate of the photo-oxidation of phenols and α-phellandrene in different solvents

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(*Received 3 March 2007; in final form 4 May 2007*)

The catalytic effect of aqueous solutions of lithium perchlorate and lithium trifluoromethanesulfonate on the photochemical oxidation of various phenols has been studied. Additionally, the increase of the yield of studied reactions has been observed in weakly alkaline aqueous solutions in comparison to the neutral ones. The analogous catalytic effect of 4 M or 2 M solutions in Et_2O and CH_2Cl_2 of lithium perchlorate and lithium trifluoromethanesulfonate on the reaction of α-phellandrene with singlet oxygen has been also observed.

Keywords: Phenols; α-Phellandrene; Photochemical oxidation

1. Introduction

The aim of the present study was to compare the effect of $LiClO_4$ and CF_3SO_3Li on rates and products of the reaction of different phenols and α-phellandrene, a cyclic diene, with singlet oxygen. We suspected that association of the diene and phenols with Li^+ would alter the balance of the possible products of these reactions. The reaction of singlet oxygen with phenols has received considerable attention both in mechanistic studies and in applications to synthetic methodology. Dye-sensitized photo-oxidations of phenols have been extensively studied by Matsuura [1,2] and, in a variety of cases, the intermediacy of $^1O_2$ has been shown by competitive inhibitors, quenching techniques and solvent isotope effects.

Wasserman [3] has shown the catalytic effect of fluoride ion in putative $^1O_2$–phenol reactions. He used *p*-cresol and a number of phenols bearing electron-withdrawing substituents. *p*-Cresol underwent photo-oxidation very slowly without fluoride, but in the presence of 1 equivalent of Bu_4NF, it was photo-oxidized within 3 h to give 4-hydroperoxy-4-methyl-2,5-cyclohexadien-1-one. However, attempts to extend this

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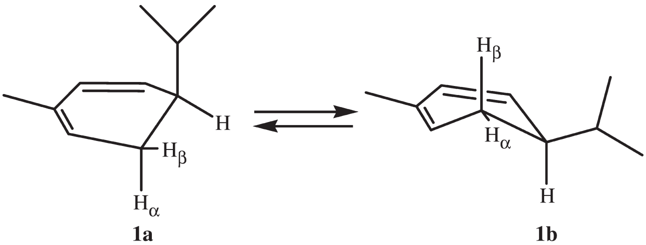
Physics and Chemistry of Liquids
ISSN 0031-9104 print/ISSN 1029-0451 online
DOI: 10.1080/00319100701434338

procedure to phenols bearing electron-withdrawing groups in the 4-position were unsuccessful.

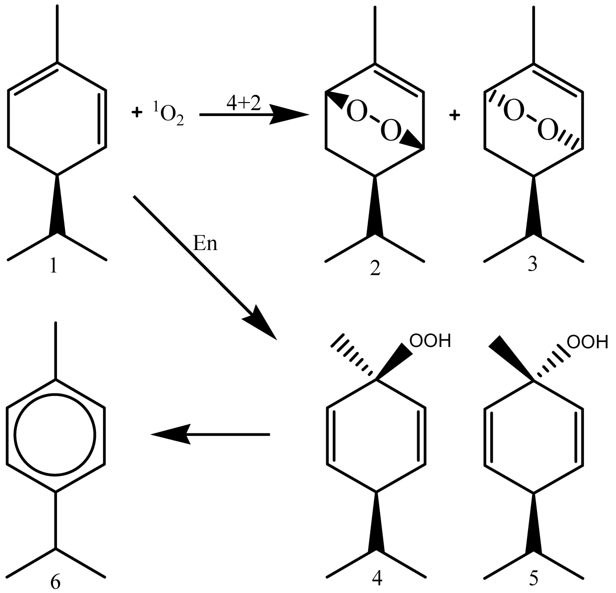
Additionally, uptake of $^1O_2$ by *p*-cresol did not occur when methylene blue was used as a sensitizer instead of Rose Bengal. Therefore, it was suggested [3] that the oxidation did not occur via a $^1O_2$ mechanism but, rather, by electron transfer with the dye.

Ohta [4] studied photo-oxidation of hindered phenols. He found that 4-hydroperoxy-2,5-cyclohexadien-1-ones were formed in good yields during 9,10-dicyanoanthracene sensitized photo-oxidation reaction of 2,4,6-trialkyl-substituted phenols. On other hand, monoalkyl-substituted phenols were photo-oxidized much slower. Hydroquinones and cyclohexa-2,5-dien-1-ones are valuable synthetic intermediates [5]. Different oxidation methods have been tested for phenols. However, photo-oxidation seems to be the simplest and the most environmentally friendly one [6]. Photo-oxidation of phenol itself leads to the hydroxylated biaryl which is an essential step in the biosynthesis of many alkaloids and other natural products [7]. Becker [8] has reported a procedure of oxidative conversion of benzofuranylidenones obtained from 4,4′-biphenylodiols into isoxindigos.

Generally, researchers believe that oxidation of phenols lacks selectivity, and hence a novel practical method for this process still waits to be explored. Recently Takaki [9] reported a selective oxidation of phenols to hydroxybenzaldehydes and benzoquinones with dioxygen catalyzed by polymer-supported copper. The possibility of application of singlet oxygen for bleaching of cellulose was studied by several authors [10a,b]. Lucia [11] analyzed the impact of different factors such as pH of the aqueous solution for the yield of photo-oxidation of phenols. It achieves the maximum value for $pH = 9.2$. Saito [2] carried out the photosensitized oxygenation of 4,6-di-t-butylresorcinol and its methyl ethers in methanol. He postulated for the first one a mechanism involving formation of the phenoxy radical intermediate as the result of hydrogen abstraction from phenol by singlet oxygen. Whereas, a mechanism involving 1,4-cycloaddition of singlet oxygen to the aromatic nucleus was proposed by him for photosensitized oxygenation of monomethyl and dimethyl ethers of 4,6-di-t-buylresorcinol. Endo [12] carried out analogous mechanistic studies based on the identification of products of the photo-oxidation of different 4-alkylphenols. He [12] examined also the solvent effect for these reactions run in methanol, acetone, and ethyl acetate. According to him, the photosensitized oxygenation of *p*-cresol proceeds much easier in methanol than in ethyl acetate. A number of reactions have recently been shown to be surprisingly susceptible to catalysis by lithium perchlorate (typically $5\,\mathrm{mol\,dm^{-3}}$ in diethyl ether) [13]. These include the rearrangement of allyl vinyl ethers [14] and of allyl stannanes [15], Diels–Alder reactions [16], the conjugate addition of silyl ketene acetals to α,β-unsaturated carbonyl compounds [17], the addition of allylstannanes to aldehydes [18a,b] and ene as well as metalloene reactions of singlet oxygen and azo enophiles [19a–f]. Also, recently Augè [20] has shown that lithium trifluoromethanesulfonate is an alternative to lithium perchlorate as a promotor in Diels–Alder reactions. The aim of the present study was to compare the reactivity of different phenols in the reaction with singlet oxygen carried out in aqueous solutions at $pH = 7$ and 9.2, and to confirm the catalytic effect of lithium perchlorate and lithium trifluoromethanesulfonate at their and α-phellandrene photo-oxidation. Matusch [21] reported that Bengal rose, tetraphenylporphine and methylene blue-sensitized photo-oxidation of α-phellandrene (**1**) (being in a solution of mixture of two conformers (**1a**) and (**1b**) (scheme 1)) carried out in methanol, dichloromethane, and isopropyl alcohol, respectively, at room



Scheme 1. Conformations **1a** and **1b** of *α*-phellandrene **1**.



Scheme 2. Products of photochemical oxidation of *α*-phellandrene.

temperature gave a mixture of the peroxides (**2**), (**3**) and hydroperoxides (**4**) and (**5**) together with small amount of other possible hydroperoxides and the aromatizatization product *p*-cymene (**6**) (scheme 2). Matusch [21] observed that the ratio of **2** : **3** products increased from 3 : 2 for reaction carried out at room temperature to 4 : 2 at −50°C.

Carless [22] reported that methylene blue-sensitized oxidation of *α*-phellandrene at −80°C in dichloromethane solution gave the two known endoperoxides (**2**) and (**3**) (65%, ratio 2 : 1), and sensitive additional products (35%) in the ratio 2 : 1. The later two compounds were clearly hydroperoxides and their spectra were consistent with cyclohexadienyl structures (**4**) and (**5**). Their samples in deuteriochloroform solution in a Pyrex tube showed little conversion (ca. 15% in 1 week) when left in the dark, but gave quantitative aromatization within few hours on exposure to sunlight. Also in the presence of traces of added acid, these hydroperoxides underwent rapid aromatization to *p*-cymene (**6**) and H_2O_2. Analogously as hydroperoxides corresponding to them alcohols were also easily transformed to *p*-cymene on contact with traces of acid, or by exposure to sunlight of their solution in chloroform.

2. Experimental

NMR spectra were recorded using a Varian Gemini 200 BP spectrometer. Details of the NMR spectra of the products from the reactions of singlet oxygen and studied phenols were discussed by other authors. Photo-oxidation reactions have been carried out in a reactor of volume equal to 5 cm^3 made from the absorption bulb through which oxygen was vigorously passed while the solution was being irradiated with light from a 400 W sodium lamp for several hours. All illuminations of phenols and α-phellandrene were carried out under the same conditions (pressure of passed oxygen, intensity of irradiation of the sample, temperature (298 K) etc. were constant). Typical examples of oxidation reactions were as follows:

- A solution of phenol (200 mg) and Rose Bengal (3 mg) in 5 cm^3 of 5 mol dm^{-3} solution of $LiClO_4$, or 10 mol dm^{-3} solution of CF_3SO_3Li in water, was vigorously saturated with oxygen while being irradiated with light from a 400 W sodium lamp for 12 h. The solvent was removed and the product was isolated by gradient chromatography (light petroleum-ethyl acetate (7/3 v/v) as eluent). It was identified by ^{1}H-NMR.
- A solution of α-phellandrene (0.2 mL) and tetraphenylporphine (3 mg) in 5 cm^3 of diethyl ether, 4 mol dm^{-3} solution of $LiClO_4$ in Et_2O or 3 mol dm^{-3} solution of CF_3Li in Et_2O was vigorously stirred under oxygen while being irradiated with light from 400 W sodium lamp. The progress of the reaction was monitored by NMR and TLC [using light petroleum-diethyl ether (8/2 v/v) as eluent]. The solvent was removed and the product was identified by ^{1}H-NMR. The peroxides (**2**) and (**3**) exhibited separate double quartets at 6.31 and 6.17 ppm corresponding to H–C(2) protons. NMR data for hydroperoxides (**4**) and (**5**) showed δ_H (200 MHz, $CDCl_3$) two overlapping multiplets at 5.98 ppm corresponding to four protons [H–C(3) and H–C(5)] of both hydroperoxides and at 5.70 ppm corresponding to another four protons [H–C(**2**) and H–C(**6**)] of (**4**) and (**5**). Studied mixture was additionally separated by a gradient chromatography using light petroleum–diethyl ether which enabled to separate mixtures of peroxides (**2**) and (**3**), hydroperoxides (**4**) and (**5**), and cymene (**6**).

The NMR spectra of most of the products from oxidation of studied phenols [3,7,23] and α-phellandrene [24] have been described by other authors, and provided the basis of the identification reported in this work. Details of compounds which have not been reported before are as follows:

4-Hydroperoxy-3,4-dimethyl-2,5-cyclohexadienone. m.p. 135–138°C. δ_H ($CDCl_3$): 1.36 (3H, s); 2.09 (3H, d, $J = 0.9$ Hz); 6.13 (1H, m); 6.22 (1H, dd, $J_1 = 9.9$ Hz, $J_2 = 1.9$ Hz); 6.97 (1H, d, $J = 9.9$ Hz); 10.18 (1H, s). δ_C ($CDCl_3$): 17.96, 26.27, 68.78, 128.34, 131.84, 153.98, 163.35, 186.22.

3. Results and discussion

Photo-oxidations of phenol, 2,6-dimethylphenol, 2,4-dimethylphenol, 3,4-dimethylphenol, and *p*-cresol have been carried out in pure water, weakly alkaline aqueous solutions of pH = 9.2, and 5M solutions of $LiClO_4$ in water, 10 M solutions of CF_3SO_3Li in H_2O, 1 M solutions of Bu_4NF in H_2O and in methanol.

Obtained results indicate that the yield of the reaction and type of products depend on pH of studied solutions and the addition of different salts which catalyze this reaction. Also studied phenols exhibit different activity in the reaction with $^1O_2$ depending on their structure. In the series of five studied phenols their reactivity is arranged in the following order phenol < 4-methylphenol < 2,6-dimethylphenol < 2,4-dimethylphenol ~3,4-dimethylphenol. Results of the oxidation of studied phenols have been compared in different solutions for the reaction carried out by 12 h under the same conditions and they have been collected in table 1.

Photo-oxidation of different phenols carried out in aqueous solutions of $LiClO_4$, CF_3SO_3Li, and in pure water of $pH = 7$ and 9.2.

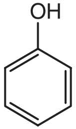
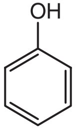
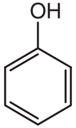
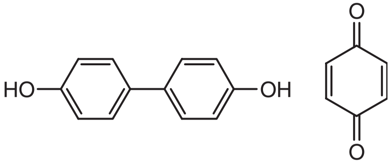
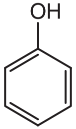
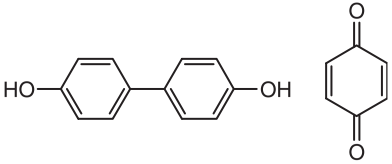
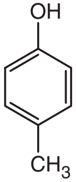
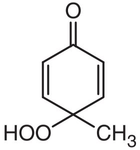
Previously Wasserman [3] observed that *p*-cresol underwent photo-oxidation in $CHCl_3$ very slowly without fluoride, but in the presence of 1-equivalent of Bu_4NF, it was photo-oxidized within 3 h to give hydroperoxide. The analogous catalytic effect has not been observed by us for reactions of phenol and 2,4-dimethylphenol with singlet oxygen carried in 1 M solutions of Bu_4NF in water and methanol. Only the slight increase of the yields of these reactions in comparison to oxidations carried out in pure solvents has been detected. Whereas, in weakly alkaline aqueous solutions we have confirmed the increase of the yield of the photo-oxidation reactions for all five studied phenols. The catalytic effect shown by $LiCLO_4$ and CF_3SO_3Li was even much stronger. Although the exact mechanism of this effect caused by lithium salts is not clear for us, it seems that it must be associated with the facilitation of the addition of $^1O_2$ to the aromatic ring.

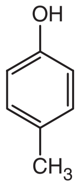
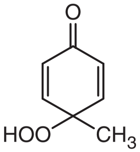
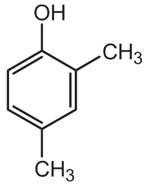
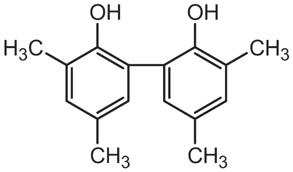
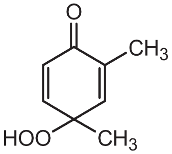
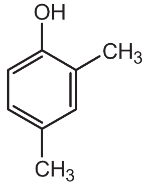
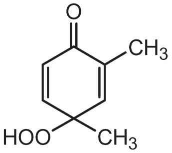
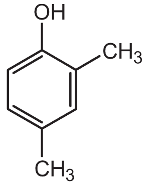
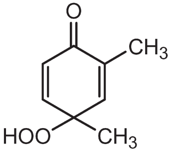
The NMR spectra of most of the products from oxidation of studied phenols were described by other authors, and they provided the basis of the identification reported in this work [3,7,23a,d] similarly as for *α*-phellandrene [24].

The reaction of *α*-phellandrene (**1**) with singlet oxygen under conditions studied by us gave two peroxides (**2**) and (**3**) by cycloaddition, and two hydroperoxides (**4**), (**5**) by ene reactions as the major products. These hydroperoxides underwent aromatization to *p*-cymene (**6**) during illumination of the reaction mixture. No considerable alteration of the balance of products was obtained with change of the solvent assuming that *p*-cymene was entirely formed from hydroperoxides (**4**) and (**5**). We were able to monitor from ^1H-NMR spectra the ratio of peroxides (**2**) : (**3**). The addition of lithium perchlorate and lithium trifluoromethanesulfonate has no effect on above mentioned ratio. We have carried out photo-oxidations of *α*-phellandrene at room temperature in 4 M solutions of $LiClO_4$ in diethyl ether, 3M solutions of CF_3SO_3Li in Et_2O, 2M solutions of CF_3SO_3Li in CH_2Cl_2 and in acetone and ethyl acetate. The ratio of peroxides (**2**) : (**3**) for reaction carried out in Et_2O was equal to 1.5. Whereas in 4 M solution of $LiClO_4$ in diethyl ether and 3M CF_3SO_3Li in Et_2O it was equal to 1.48 and 1.51, respectively. In CH_2Cl_2 and in 2 M solution of CF_3SO_3Li in CH_2Cl_2 monitored ratio was equal to 1.47 and 1.43, respectively. Similarly, in ethyl acetate and acetone the discussed ratio was equal to approximately 1.45. It seems to indicate that the change of polarity of the solvent and the addition of lithium salt has no influence on the ratio of peroxides (**2**) : (**3**). However, the catalytic salt effect illustrated by the decrease of the time of reaction required for complete consumption of *α*-phellandrene and a small increase of the relative yield of peroxides (**2**) and (**3**) was observed (table 2).

Previously [25] we have shown that the catalytic role of $LiClO_4$ in the case of photo-oxygenation of tetraallyltin cannot be explained by possible variations in the

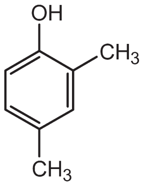
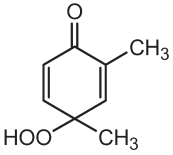
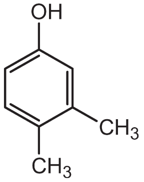
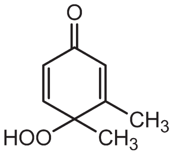
Table 1. Photo-oxidation of different phenols carried out in aqueous solutions of $LiClO_4$, CF_3SO_3Li, and in pure water of pH = 7 and 9.2.

Compound	Solvent	Product	Time of irradiation (h)	Yield of the reaction (%)
	H_2O pH = 7		12	1, 2
	H_2O pH = 9.2		12	2
	5 M $LiClO_4$ H_2O	 (44:56)	12	2
	10 M CF_3CO_3Li H_2O	 (33:67)	12	6
	H_2O pH = 7		12	3

	10 M CF_3SO_3Li H_2O		12	15
	H_2O pH = 7	  (13:87)	12	70
	H_2O pH = 9.2		12	100
	5 M $LiClO_4$ H_2O		8	100

(*Continued*)

Table 1. Continued.

Compound	Solvent	Product	Time of irradiation (h)	Yield of the reaction (%)
	10 M CF_3SO_3Li H_2O		4	100
	H_2O pH = 7		12	70

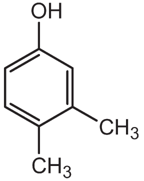
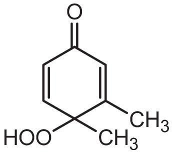
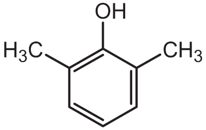
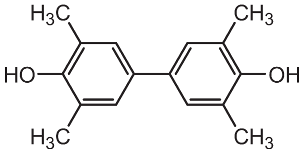
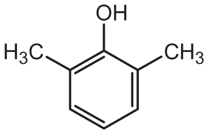
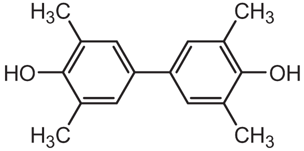
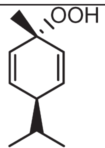
	H_2O pH = 9.2		12	100
	H_2O pH = 7		12	19
	10 M CF_3SO_3Li H_2O		12	90

Table 2. Photochemical oxidation of phellandrene.

Solvent	Yield of obtained products (%)				Time of irradiation (min)
	 2	 3	 4 +  5	 6	
Et_2O	36.7	24.4	20.2	18.6	60
4 M $LiClO_4$, Et_2O	37.1	25.0	21.3	16.6	35
3 M CF_3SO_3Li, Et_2O	42	27.8	9.1	21.0	15
CH_2Cl_2	34.9	23.7	29.0	12.4	60
2 M CF_3SO_3Li, CH_2Cl_2	41.2	28.8	21.0	9.0	15
CH_3COCH_3	35.5	24.5	15	25	60
CH_3COOEt	35.5	24.5	5	35	60

concentration of $^1O_2$ under heterogenous conditions, of $^1O_2$, or of its lifetime. We suspect that the mechanism of the catalysis by lithium salts of photo-oxidation of α-phellandrene is associated with the facilitation of the formation of the polar intermediate during the studied reaction.

References

[1] T. Matsuura, H. Matsushima, S. Kato, I. Saito. *Tetrahedron*, **28**, 5119 (1972).
[2] N. Saito, N. Yoshimura, T. Arai, K. Amura, A. Nishinaga, T. Matsuura. *Tetrahedron*, **28**, 5131 (1972).
[3] H.H. Wasserman, J.P. Pickett. *Tetrahedron*, **41**, 2155 (1985).
[4] S. Futamura, K. Yamazaki, H. Ohta, Y. Kamiya. *Bull. Chem. Soc. Jpn*, **55**, 3852 (1982).
[5] D. Lotta, M. Saindane, C. Barnum. *J. Am. Chem. Soc.*, **103**, 3224 (1981).
[6] M. Oelgemöller, C. Jung, J. Ortner, J. Mattay, E. Zimmermann. *Green Chem.*, **7**, 35 (2005).
[7] G. Sartori, R. Maggi, F. Bigi, A. Arienti, G. Casnati. *Tetrahedron*, **48**, 9483 (1992).
[8] H.D. Becker, H. Lingnert. *J. Org. Chem.*, **47**, 1095 (1982).
[9] K. Takaki, Y. Shimasaki, T. Shishido, K. Takehira. *Bull. Chem. Soc. Jpn*, **75**, 311 (2002).
[10] (a) C. Crestinin, M. D'Auria, *J. Photochem. Photobio.*, **A 101**, 69 (1996); (b) R. Ruggiero, A.E.H. Machado, A. Castellan, S. Grelier, *J. Photochem. Photobio.*, **A 110**, 91 (1997).
[11] L.A. Lucia. *The Spectrum*, **14**, 8 (2001).
[12] K. Endo, K. Seya, H. Hikino. *Tetrahedron*, **45**, 3673 (1989).
[13] A. Heydari. *Tetrahedron*, **58**, 6777 (2002).
[14] P.A. Grieco, J.D. Clark, C.T. Jagoe. *J. Am. Chem. Soc.*, **113**, 5488 (1991).
[15] Y. Nishigaichi, A. Takuwa, K. Iihama, N. Yoshida. *Chem. Lett.*, **10**, 693 (1991).
[16] P.A. Grieco, J.J. Nunes, M.D. Gaul. *J. Am. Chem. Soc.*, **112**, 4595 (1990).
[17] P.A. Grieco, R.J. Cooke, K.J. Henry, J.M. VanderRoest. *Tetrahedron Lett.*, **32**, 4665 (1991).
[18] (a) K.J. Henry, P.A. Grieco, C.T. Jagoe, *Tetrahedron Lett.*, **33**, 1817 (1992); (b) Y. Nishigaichi, N. Nakano, A. Takuwa, *J. Chem. Soc., Perkin Trans.* **1**, 1203 (1993).
[19] (a) A.G. Davies, W.J. Kinart, *J. Chem. Soc., Perkin Trans.* **2**, 2281 (1993); (b) W.J. Kinart, E. Śnieć, I. Tylak, C.M. Kinart, *Phys. Chem. Liq.*, **38**, 193 (2000); (c) W.J. Kinart, C.M. Kinart, I. Tylak, *J. Organomet. Chem.*, **608**, 49 (2000); (d) W.J. Kinart, C.M. Kinart, I. Tylak, K. Mikołajczuk, *Phys. Chem. Liq.*, **40**, 405 (2001); (e) W.J. Kinart, R. Nazarski, C.M. Kinart, Q.T. Thuong, R. Oszczęda, *Synth. Commun.*, **35**, 1059 (2005); (f) W.J. Kinart, C.M. Kinart, *J. Organomet. Chem.*, **691**, 1441 (2006).
[20] J. Augé, R. Gil, S. Kalsey, N. Lubin-Germain. *Synlett*, 877 (2000).
[21] R. Matusch, G. Schmidt. *Angew. Chem. Int. Ed. Eng.*, **27**, 717 (1988).
[22] R. Atkins, H.A.J. Carless. *Tetrahedron Lett.*, **28**, 6093 (1987).

[23] (a) V. Balogh, M. Fétizon, M. Golfier, *J. Org. Chem.*, **36**, 1339 (1971); (b) I. Pallahi, A. Toró, G. Horwáth, *J. Org. Chem.*, **61**, 6530 (1999); (c) K. Takahashi, T. Suzuki, K. Akiyama, Y. Ikegami, Y. Fukazawa, *J. Am. Chem. Soc.*, **113**, 4576 (1991); (d) V. Courtois, R. Barhdadi, M. Troupel, *J. Périchon, Tetrahedron*, **53**, 11569 (1997).
[24] R. Matusch, G. Schmidt. *Helvetica Chim. Acta*, **72**, 51 (1989).
[25] W.J. Kinart, I. Tylak, C.M. Kinart. *J. Chem. Res.*, **S**, 46 (1999).