Pergamon

Tetrahedron 55 (1999) 5903–5908

TETRAHEDRON

Catalytic Selective Oxidation of Alkyl Arenes to Aryl *tert.* Butyl Peroxides with TBHP over Ru-Exchanged Montmorillonite K10

Milind D. Nikalje and A. Sudalai*

Division of Organic Chemistry,
National Chemical Laboratory, Pune - 411008. India

Received 9 December 1998; revised 23 February 1999; accepted 11 March 1999

Abstract : A mild and efficient catalytic method for the benzylic oxidation of alkyl arenes to the corresponding *tert.* butyl aryl peroxides is described using a catalytic amount of reusable solid, Ru^{III}-exchanged Montmorillonite K10 and 70% *tert.* butyl hydroperoxide (TBHP) as oxidant. © 1999 Elsevier Science Ltd. All rights reserved.

Key words: Arene, Peroxidation, Peroxide, Clay, Ruthenium.

INTRODUCTION

Organic peroxides are involved in many biological processes including development of rancidity in fats, loss of activity of vitamin products and firefly bioluminescence. Some biological products contain a peroxide group *e.g.* the natural product, qinghaosu is a 1,2,4-trioxane that possesses antimalarial properties and ascaridole is an endoperoxide that possesses sedative, analgesic, antirheumatic and antihelmintic properties [1]. Organic peroxides are also involved in gum formation in lubricating oils, prepolymerization of some vinyl monomers and degradation of olefin polymers. The importance in synthetic application of these peroxides lies in their ability to decompose to valuable compounds [2].

SYNTHESIS OF ORGANIC PEROXIDES

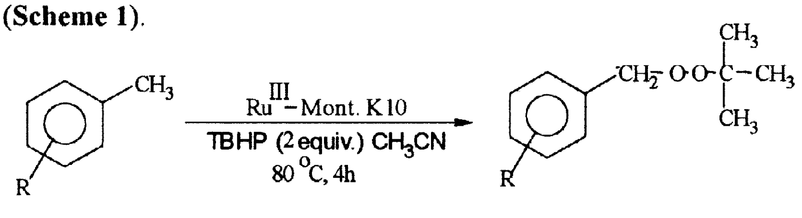
The selective oxidation at the benzylic C-H bond of alkyl arenes constitutes a potential route for the functionalization of alkyl arenes into oxygenated derivatives such as peroxides, alcohols, aldehydes, ketones, and acids. The reaction selectivity to produce specific oxygenated derivatives such as peroxides is of crucial importance. Kharasch *et al.* reported that oxidation of organic compounds containing activated C-H bonds with alkyl hydroperoxide under catalysis by metal ions such as Cu(I), Mn(II), or Co(II) leads to the formation of dialkyl peroxides [3]. However, this system suffers from a parallel non-productive catalytic decomposition of TBHP which causes rather low yields of the peroxide product. Muzart *et al.* have recently reported a *tert.* butyl peroxidation ot tertiary benzylic carbons (Ph_3CH) with aq. TBHP catalyzed by chromium oxide [4]. Highly toxic chromium residues coupled with low selectivity to the *tert.* butyl peroxy product make this method a less preferred one. Sasson *et al.* have reported tertiary peroxidation of tetralin using $CuCl_2$ as catalyst under phase transfer conditions [5]. However, the maximum conversions achieved were only 50% and the product selectivity was found to be sensitive to the reaction conditions. More recently, Minisci *et al.* have reported the synthesis of mixed peroxides under Gif-Barton oxidation (Fe^{III}, TBHP, pyridine, AcOH) of alkyl benzenes [6]. However, the ratio of substrate to oxidant needed to be quite high for a moderate conversion. Several other

PII: S0040-4020(99)00252-5

catalytic methods have been developed for the benzylic oxidation using soluble ruthenium salts as well as reusable catalysts such as Cr-PILC [7], Cr-APO [8] and Cr-MCM-41 [9] in combination with reoxidants such as peracids and TBHP. However, the benzylic oxidations using soluble Cr and Ru catalysts lead to over oxidized products such as ketones and acids using a large excess of peracids or TBHP as oxidants. Further, the known methods to obtain unsymmetrical peroxides from alkyl bromides or mesylates under strong basic conditions did not always lead to pure peroxides [10]. Most of the existing methods employ homogeneous catalysts and show poor selectivity in terms of product distribution. Therefore, it assumes great importance to have effective control over selectivity in such reactions.

CLAY AS CATALYST

Due to their Bronsted and Lewis acidities both in their natural and ion-exchanged forms, clays function as efficient catalysts for various organic transformations [11]. Recently, we have reported the exchange of various transition metals such as Pd, Cu, Rh, Mn *etc.* with Montmorillonite K10 clay and found that such clay catalysts showed excellent activity for many C-C and C-N bond forming reactions [12,13]. In continuation, we wish to describe in detail our results on the chemistry of the oxidation of alkyl arenes wherein the unique role of Ru^{III}-exchanged Mont K10 clay in controlling the reaction selectivity to peroxides using aq. TBHP as oxidant has been demonstrated (**Scheme 1**).



R = H, CH3, Cl etc

Scheme 1

RESULTS AND DISCUSSION

Initially, a systematic investigation of the oxidation of toluene with different types of metal exchanged clays using aq. TBHP as oxidant was undertaken (Table 1). The results clearly show that the Ru^{III}-exchanged Mont K10–TBHP combination exhibits higher activity and selectivity as compared to other Mn and Cu-exchanged Mont K10 catalysts. It was also found that both solvent (CH_3CN) and TBHP (2 equiv.) are critical

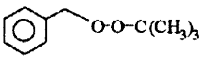
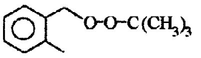
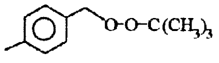
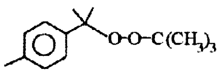
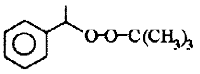
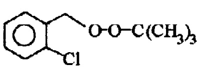
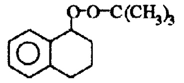
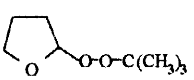
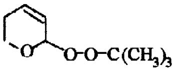
Table 1: Selective oxidation of toluene to benzyl *tert.* butyl peroxide with TBHP: Effect of catalyst, the solvent and oxidant.

Entry	Catalyst	Surface area^a (m^2/g)	Solvent	TBHP^b Equiv.	Product^c (%)
1	Ru-Mont K10	258	CH_3CN	2	60
2	Mn-Mont K10	255	CH_3CN	2	7
3	Cu-Mont K10	238	CH_3CN	2	14
4	$RuCl_3$- hydrate	--	CH_3CN	2	0
5	Ru-Mont K10	258	MeOH	2	30
6	Ru-Mont K10	258	Acetone	2	42
7	Ru-Mont K10	258	CH_3CN	1.1	2
8	Ru-Mont K10	258	CH_3CN	1.7	45
9	Ru-Mont K10	258	CH_3CN	2.2	62

(a)Determined by Brunauer-Emmette-Teller (BET) method (b) TBHP equiv. is based on substrate used (c) Isolated yield after chromatographic purification (silica gel, pet ether) for a high yield of product formation while $RuCl_3$ under homogeneous conditions failed to activate toluene under similar conditions.

In order to study the scope and limitation of this reaction, various alkyl arenes were subjected to oxidation under the influence of Ru^{III}-exchanged Mont. K10 (Table 2) and the reaction was found to be quite general. The reactivity pattern of different arenes and cyclic ethers towards TBHP under the present conditions follows the sequence: $RO\text{-}CH_2 > R_3CH > R_2CH_2 > RCH_3$. A remarkable feature of the present oxidation process is that one of the methyl groups is selectively oxidized in xylenes, while in the case of p-cymene, the oxidation occurs at the C-H group in preference to the CH_3 group. However, electron rich substrates such as isobutylbenzene and fluorene are oxidized exclusively at the benzylic positions to give the corresponding ketones in high yields. Also noteworthy is the selective oxidation occurring at the α-position of THF and 3,4-dihydropyran to give the corresponding *tert.* butyl peroxides in moderate yields (Table 2). The isolated yields of the peroxides are generally higher compared to the literature methods [14].

Table 2 : Oxidation of benzylic C-H bonds with 70 % TBHP over Ru-Mont. K10 clay.

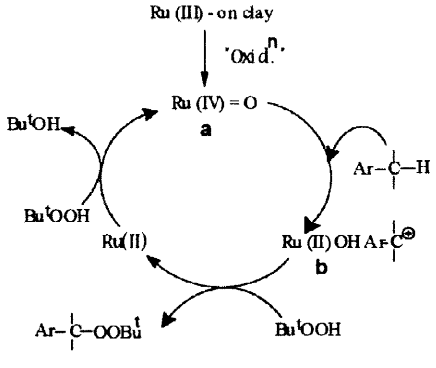
Entry	Substrate	Products		Yields (%)[a]
a	Toluene		**(1)**	60
b	o-Xylene		**(2)**	76
c	p-Xylene		**(3)**	47 (29)[b]
d	p-Cymene		**(4)**	90
e	Ethylbenzene		**(5)**	54 (28)[c]
f	o-Chlorotoluene		**(6)**	76
g	Tetralin		**(7)**	50
h	Tetrahydrofuran		**(8)**	45
i	3,4- Dihydropyran		**(9)**	70
j	Isobutylbenzene	Isobutyrophenone		94
k	Fluorene	Fluorenone		100
l	p-Cresol acetate	4–Acetoxybenzoic acid		50
m	Mesitylene	3,5-Dimethylbenzoic acid		94

(a) Isolated yield after column chromatographic purification. Yield in parenthesis refers to (b) *p*-Toluic acid, (c) Acetophenone

The catalyst from the reaction mixture was recovered by simple filtration and was successfully reused for oxidation of toluene and it was found that a lower yield (55%) of the product was realized. In order to check the leaching of ruthenium from the catalyst the aqueous layer of the reaction mixture was analyzed for the presence of Ru metal by atomic absorption spectroscopy and it was found that no Ru had leached from the catalyst.

MECHANISM

The proposed mechanism of the Ru(III) catalyzed oxidation is shown in **Scheme 2**. The first step involves the oxidation of the metal in Ru(III) on clay with TBHP to give oxoruthenium (IV) species **a** [15, 16]. The cyclic voltammetry (CV) measurements confirm this one electron redox behavior. The CV of Ru(III)-exchanged Mont. K10 clay recorded at a scan rate 100 mV/sec shows a reversible peak at –131.6 mV (vs SCE). We attribute this, after the literature comparison [17] to Ru(III)/Ru(IV) redox process. The voltammograms are quite stable over many cycles indicating that the Ru(III) ions are stabilized in the clay matrix. The oxoruthenium (IV) species **a** then abstracts hydride ion from the benzylic position, thereby Ru(IV) is reduced to Ru(II) species with the simultaneous generation of reactive intermediate carbocation **b** [18, 19, 20]. The reaction of 1 mole equiv. of TBHP with the carbocation **b** affords the aryl *tert.* butyl peroxide. The final step involves the simultaneous oxidation of Ru(II) back to the original Ru(IV) species **a** to complete the catalytic cycle, thus explaining the overall requirement of 2 molar equiv. of TBHP for oxidations. A similar argument can be made for the oxidation of the α-C-H bond of the cyclic ethers (entries h & i). Further, the formation of both acids and ketones could be explained by oxidation of the corresponding benzylic alcohols presumably formed by the competitive reaction of a water molecule with the respective stable carbocations (**Scheme 2**).



Scheme 2

CONCLUSION

This study has demonstrated that Ru^{III}-exchanged Mont. K10 is an efficient and reusable solid catalyst for the activation of benzylic and α-C-H bonds of cyclic ethers using 70% TBHP as the oxidant to afford unsymmetrical *tert.* butyl peroxides in high yields.

Acknowledgment: We are thankful to CSIR (New Delhi) for the award of JRF. We are also thankful to the Director, NCL for providing infrastructure facilities.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer Infrared model 137-E. ^{1}H & ^{13}C NMR spectra were taken on a Bruker 200 MHz instrument. The chemical shifts were reported with TMS as the internal standard. The mass spectra (MS) were recorded on a automated Finnigan MAT 1020 C mass spectrometer using ionisation energy of 70 eV. Microanalyses were performed at the Organic Chemistry Division, NCL.

Preparation and characterization of Ru, Mn, Cu- exchanged montmorillonite K10: Ru, Mn and Cu-exchanged montmorillonite K10 clay catalysts were prepared by exchanging the clay with dilute solutions of $RuCl_3$, $Mn(NO_3)_2.6H_2O$ and $Cu(NO_3)_2$ respectively. For example, a mixture containing $RuCl_3$ (0.3g) and clay (25g) in distilled water (600 ml) was stirred vigorously at room temperature for 24 h. It was centrifuged and the clay was washed repeatedly with distilled water until the discarded filtrate was free from Cl^- ions. Finally, the clay was dried at 110 °C for 12 h. The metal content of the catalyst was determined by Electron Disperse X-ray microscope (EDX) (Kevex, US) connected to JEOL (JSM 5200) Scanning Electron Microscope (SEM). The surface area of Ru^{III}-exchanged Mont. K10, Mn^{II}-exchanged Mont. K10 and Cu^{II}-exchanged Mont. K10 being 258, 255 and 238 m^2/g respectively (BET method). The XRD pattern and FT-IR spectra of these samples show that they are crystalline and no significant differences were observed among their structures. However, definite information about the nature of the metal species present in the catalyst could be obtained from Cyclic Voltammetry (CV) and X-ray Photoelectron Spectroscopy (XPS). The XPS of Ru^{III}-exchanged Mont. K10 clay shows two peaks at 282.2 and 286.2 eV for Ru-$3d_{5/2}$ and $3d_{3/2}$ levels which can be assigned to the Ru^{III} oxidation state.

General procedure for oxidation of the alkyl arenes to *tert.* butyl peroxide: A mixture of alkyl arene (5 mmol), 70% TBHP (1.3 ml, 10 mmol) and Ru-clay (0.053 g, 10% wt) in acetonitrile (10 ml) was refluxed for 4h. After completion of the reaction (TLC monitoring, 5% ethyl acetate in pet. ether), the catalyst was separated by filtration and the reaction mixture poured into water (15 ml) followed by extraction with ethyl acetate (3 x 20ml) to give the crude product which was subsequently purified by column chromatography (1% ethyl acetate in pet. ether) to afford aryl *tert.* butyl peroxide.

1,1-Dimethylethylphenylmethyl peroxide (1): Yield : 60 %; Liquid; bp, 55-58°C/0.2mm Hg (lit.[14] 60-65 °C/0.3mm Hg); IR ($CHCl_3$, cm^{-1}) : 2960, 2900, 1690, 1450, 1360, 1240, 1200, 1020, 880, 750; ^1H NMR (200 MHz, $CDCl_3$) : δ 1.25 (9H, s, CH_3), 4.95 (2H, s, CH_2), 7.1-7.2 (5H, s, Ph); MS : m/z (% rel. intensity) 180 (M^+, 32), 105 (22), 91 (90), 77 (74), 65 (18), 57 (100). Anal. : $C_{11}H_{16}O_2$: required : C, 73.30; H, 8.95; Found : C, 73.12, H, 8.80 %.

1,1-Dimethylethyl-1-(2-methylphenyl)methyl peroxide (2): Yield : 76 %; Liquid; bp,78-81 °C/0.2mm Hg; IR ($CHCl_3$, cm^{-1}) : 3020, 2980, 1420, 1370, 1260, 1190, 1010, 900, 740; ^1H NMR (200 MHz, $CDCl_3$) : δ 1.25 (9H, s, CH_3), 2.4 (3H, s, CH_3), 5.0 (2H, s, CH_2), 7.2-7.4 (4H, m, Ph); MS : m/z (% rel. intensity) 194 (M^+,1), 148 (1), 133 (1.5), 119 (10), 105 (100), 91 (55), 77 (38), 65 (20), 57 (40); Anal.: $C_{12}H_{18}O_2$, required : C, 74.19; H, 9.34; Found : C, 74.20; H, 9.26 %.

1,1-Dimethylethyl –1-(4-methylphenyl)methyl peroxide (3): Yield : 47 %; Liquid; bp, 65-68°/0.2mm Hg (lit.[21] 65°C/0.2mm Hg), IR ($CHCl_3$, cm^{-1}); 3020-2800, 2620, 2440, 1370, 1320, 1220, 1080, 1040, 950, 880, 770; ^1H NMR (200 MHz, $CDCl_3$) : δ 1.25 (9H, s, CH_3), 2.35 (3H, s, CH_3), 4.8 (3H, s, CH_2); 7.2 (2H, d, J=4.7 Hz, 2H), 7.4 (2H, d, J=4.7 Hz, 2H); MS : m/z (% rel. intensity) 194 (20), 178 (1), 137 (2), 119 (38), 105 (100), 91 (80), 77 (42), 73 (20), 65 (45), 57 (73); Anal. : $C_{12}H_{18}O_2$, requires : C, 74.19; H, 9.34; Found : C, 74.19; H, 9.25 %.; p-Toluic acid was also obtained in 29% yield and characterized by mp, IR and ^1H NMR.

1,1-Dimethylethyl-1-methyl(4-methylphenyl)ethyl peroxide (4): Yield : 90%; Liquid; bp, 70-73°C/0.2mm Hg; IR($CHCl_3$, cm^{-1}): 2950, 1650, 1350, 1200, 1060, 850, 750; ^1H NMR (200 MHz, $CDCl_3$) : δ 1.25 (9H, s, CH_3), 1.4 (3H, s, CH_3), 1.65 (3H, s, CH_3), 6.25 (2H, d, J=9.4 Hz), 6.85 (2H, d, J=9.4 Hz); MS : m/z (% rel. intensity) 222 (M^+, 8), 172 (15), 147 (24), 133 (100), 199 (28),105 (20), 91 (30), 77 (4), 65 (10), 57 (8); Anal. : $C_{14}H_{22}O_2$, requires : C, 75.63, H, 9.97; Found: C, 75.66, H, 9.89 %.

1,1-Dimethylethyl-1-phenylethyl peroxide (5): Yield : 54 % ; Liquid; bp, 54-57°C/1mm Hg (lit.[22] 48-52°C/0.9mm Hg), IR ($CHCl_3$, cm^{-1}) : 3100, 2800, 1440, 1370, 1220, 1070, 880, 760; ^1H NMR (200 MHz, $CDCl_3$) : δ 1.25 (9H, s, CH_3), 1.2 (3H, d, J=4.7 Hz, CH_3), 5.0 (1H, q, J=4.7 Hz, CH), 7.3-7.4 (5H, s, Ph); MS : m/z (% rel. intensity); 194 (M^+, 1), 179 (1.7), 163(2) 133(5), 121(33.5), 105 (100), 91 (14), 77 (52), 65 (2), 57(4); Anal. : $C_{12}H_{18}O_2$ requires : C, 74.19; H, 9.34; Found : C, 74.19; H 9.25% and acetophenone was also obtained in 28% yield and was characterized by IR and ^1H NMR.

1,1-Dimethylethyl(2-chlorophenyl)methyl peroxide (6): Yield : 76 %; Liquid; bp, 45-49°C/0.1mm Hg; IR($CHCl_3$,cm^{-1}): 3000, 2900, 1580, 1430, 1350, 1200, 1030, 920, 860; ^1H NMR (200 MHz, $CDCl_3$) : δ 1.25 (9H, s, CH_3), 5.2 (2H, s, CH_2), 7.05-7.44 (4H, m, Ph) MS : m/z (% rel. intensity) 214 (M^+, 12), 124 (1), 125 (40), 110 (8), 111 (18), 89 (5), 77 (25), 63 (1), 57 (100); Anal. : $C_{11}H_{15}ClO_2$. requires : C, 61.54; H, 7.04, Cl, 16.51; Found : C, 61.65; H, 6.99; Cl, 16.56 %.

1-(*tert.* Butylperoxy)tetralin (7): Yield : 50 %; Liquid; bp,110-112°C/1-2mm Hg; IR ($CHCl_3$, cm^{-1}) : 3020-2800, 1610, 1440, 1370-1320, 1220, 1080, 1040, 950, 880, 770; ^1H NMR (200 MHz, $CDCl_3$) δ 1.25 (9H, s, CH_3), 1.7-2.0 (2H, m, CH_2), 2.3-2.4 (2H, m, CH_2), 2.6-2.8 (2H, m, CH_2), 5.0 (1H, t, J=14.1 Hz, CH), 7.1-7.3 (3H, m, Ph), 7.5(1H, m, Ph); MS : m/z (% rel. intensity) 220 (M^+, 1), 146 (4), 130 (100), 115 (10), 103 (1), 91 (20), 77 (2), 65 (2), 57 (2); Anal.: $C_{14}H_{20}O_2$. requires : C, 76.33; H, 9.15; Found : C, 76.34; H, 9.08%.

2-(*tert.* Butylperoxy)tetrahydrofuran (8): Yield : 45 %; Clear liquid; bp, 40-45°C/8-10mm Hg; IR ($CHCl_3$, cm^{-1}) : 2960-2840, 1430, 1350, 1220, 1180, 1110, 1060, 960-910, 850; ^1H NMR (200 MHz, $CDCl_3$), δ 1.25 (9H, s, CH_3), 1.7-2.0 (4H, m, CH_2), 3.95 (2H, t, J=14.1Hz, CH_2), 5.5 (1H, t, J=4.7 Hz, CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 24.2, 26.1, 30.3, 67.4 80.7, 106.8.; MS : m/z (% rel. intensity) 144 (M^+, 1), 128 (12), 115 (23), 89 (8), 71 (100), 57 (48), 55 (40); Anal. : $C_8H_{16}O_3$. requires : C, 59.98, H, 10.07, Found : C, 59.98, H, 9.97 %.

2-(*tert.* Butylperoxy)-3,4-dihydropyran (9): Yield : 70 %; Liquid; 58-61°C/8-10 mm Hg; IR ($CHCl_3$, cm^{-1}) : 2910, 1440, 1370, 1250, 1200, 1050; ^1H NMR (200 MHz, $CDCl_3$), δ 1.25 (9H, s, CH_3), 1.5-1.75 (4H, m, CH_2), 3.6 (1H, m, CH=), 4.0 (1H, m, CH=), 5.0 (1H, t, J=9.4 Hz, CH); MS : m/z (% rel. intensity) 140 (M^+, 1), 132 (5), 119 (18), 85 (92), 73 (25), 67 (50), 57 (100); Anal. : $C_9H_{16}O_3$, requires : C, 62.76; H, 9.36, Found :C, 62.77;H, 9.28%.

References

[1] Swern D., *Organic peroxides*, vol. 1, New-York, Wiley-Interscience, **1970**, p 3.

[2] Luberoff, B. J., Simmons T. S. US Patent 1977, 63017842

[3] Kharasch M. S.; Fono A.; *J. Org. Chem.* **1959**, 72, 24.

[4] Muzart J., Ajjou A. N'ait.; *J. Mol. Catal.* **1994**, 92, 277.; *ibid.* **1991**, 66, 155,.; *ibid.* **1994**, 92, 141.

[5] Liron Feldberg, Sasson Yoel.; *Tetrahedron Lett.* **1996**, 37, 2063-2066.

[6] Minisci F., Fontana F., Araneo-S Recupero F. *J. Chem. Soc. Chem. Commun.* **1994**, (16), 1823.

[7] Choudhary B. M., Bhuma P. V., Swapna V. , *J. Org. Chem.* **1992**; 57; 5841.

[8] Sheldon R. A., Chen J. D., Dakka J., Neeleman E. *Study. Surf. Catal.* **1994**,; 83; 407.

[9] Das T.K., Chaudhary K., Nandanan E., Chandwadkar A.J., Sudalai A., Ravindranathan T., Sivasankar S., *Tetrahedron Lett.* **1997**; 38; 3631.

[10] Bourgeosis M. J., Montaudon E., Maillard B., *Systhesis*, **1989**, 700.

[11] Cornelis A., Laszlo P., *Synlett*, **1994**, 155.

[12] Ramchandani R. K., Uphade B. S., Vinod M. P., Wakharkar R. D., Choudhary V. R., Sudalai A., *Chem. Commun.* **1997**, 2071.

[13] Madan Mohan J. Uphade B. S., Choudhary V. R. Ravindranathan T., Sudalai A., *Chem. Commun*, **1997**, 1429.

[14] Filliatre par C., Courret P. et Lalande R. *Bull. Soc. Chim. Fr.*, **1976**, 1477.

[15] Marmion M. E., Takeuchi K. J., *J. Am. Chem. Soc.* **1988**, 110, 1472.

[16] Roecker, Meyer T. J. *J. Am. Chem. Soc.* **1987**, 109, 746.

[17] Llopis J. I., Tordesillas I. M. in *Encyclopaedia of Electrochemistry of the Elements*, Bard A. J., New York, Marcel Dekker Inc. **1994**, 6, 277.

[18] Murahashi S. I., Oda Y., Naota T., Kuwabara T., *Tetrahedron Lett.* **1993**, 34, 1299.

[19] Sasson Y., Zappi G. D., Neuman R., *J. Org. Chem.* **1986**, 51, 2880.

[20] Lee D. G., Den Engh M. V., *Can. J. Chem.* **1972**, 50, 2000.

[21] Kharasch M. S. Fono A., *J. Org. Chem.* **1959**, 24, 72.

[22] Ballard D. H. Bloodworth A. J. *J. Chem. Soc.* (C) , **1971**, 945.