Solvent-Free and Selective Oxidation of Hydroxy Groups to their Corresponding Carbonyl Functions with Ferric Nitrate Activated by Heteropoly Acids

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Abstract: Keggin-type heteropoly acids revealed high catalytic activity for swift and selective oxidation of various hydroxy functionalities to the corresponding carbonyl groups using ferric nitrate as an oxidant under mild and solvent-free conditions. We have found that the catalytic activities of the heteropoly acids were much higher than mineral or solid acids such as sulfuric acid, *p*-toluenesulfonic acid, triflic acid, acidic Amberlyst-15, Montmorillonite-K10 clay, and HY-zeolite.

Key words: alcohols, carbonyl compounds, ferric nitrate, heteropoly acids, oxidations

Carbonyl compounds in the fine chemicals industry are precursors with wide applicability from drugs to fragrances. The oxidation of alcohols to carbonyl products is an important transformation in organic chemistry,¹ which has received the most attention over the years, especially in search of versatile and selective reagents in catalytic applications.² Several methods are known for selective oxidation of alcohols to the corresponding carbonyl compounds. Swern oxidation,³ Dess–Martin oxidation,⁴ and various metal reagents⁵ are employed for this purpose. However, they are not free from some disadvantages and there is still a need for new methods. The main requirements are simplicity of the method, selectivity, in particular with regard to over-oxidation of carbonyl compounds, effectiveness, and mildness of the reaction.

The importance and full characterization of various heteropoly acids (HPAs) and their properties have been reviewed.⁶ A large number of recent reports concerning the catalytic activity of Keggin-type heteropoly acids and polyoxometalates for the oxidation of organic substrates are available in the literature.⁷ Solutions of these materials exhibit very strong Brønsted acidity with acid strengths more than mineral acids.8 Solid HPAs possess also Brønsted acidity and are stronger than conventional solid acids such as SiO₂/Al₂O₃, H₃PO₄/SiO₂, and those of zeolites including HX, HY and H-ZSM-5 (Si/Al = 40).⁹ Among heteropoly acids, polytungstic acids are the most widely used catalysts owing to their high acid strengths, thermal stabilities, and low reducibilities. Most of HPA catalysts are environmentally friendly and regarded as promising green catalysts.¹⁰ It is evident that the application of heteropoly

Synthesis 2003, No. 3, Print: 28 02 03. Art Id.1437-210X,E;2003,0,03,0408,0412,ftx,en;T08802SS.pdf. © Georg Thieme Verlag Stuttgart · New York ISSN 0039-7881 acids is very high and it is in the beginning of its growth in organic chemistry.

We have recently started studies upon new catalytic properties of heteropoly acids, especially the tungstophosphoric acid ($H_3PW_{12}O_{40}$) which is a cheap, reusable, heterogeneous and easily available catalyst. We have already used catalytic amounts of this compound for the oxidation of aromatic amines to nitro compounds with sodium perborate in micellar media,^{11a} thioacetalization and transthioacetalization reactions,^{11b} its cesium salt for regioselective bromination of aromatic compounds,^{11c} and selective *O*-trimethylsilylation of a wide variety of alcohols and phenols using easily available hexamethyldisilazane (HMDS) under solvent-free conditions.^{11d}

Metal nitrates supported on various inorganic supports have been used as oxidizing agents.¹² Iron(III) nitrate supported on silica gel (Silfen),^{12a–e} iron(III) nitrate or copper(II) nitrate supported on K10-clay (Clayfen or Claycop),^{12f–i} are the reagents employed for the oxidation processes. However, the stability of these reagents faces problems.^{12k,1} Recently, ferric nitrate mixed with HZSM-5 zeolite (Zeofen) has been successfully employed for the oxidation of various alcohols in solution and also in the absence of solvent under microwave irradiation.¹³

Now we report the use of ferric nitrate (1 mol) in the presence of tungstophosphoric acid (H_3PW , 0.1 mol), as a catalyst for the simple, swift, and selective oxidation of a wide variety of primary, secondary, and benzylic alcohols into their corresponding carbonyl compounds under mild and solvent-free conditions.

Effect of Catalyst

Ferric nitrate nonahydrate, an abundant, cheap, non-toxic and commercially available can be used as an oxidant in the presence of catalytic amounts of heteropoly acids or polyoxometalates. Primarily, oxidation of benzyl alcohol, as a model compound, was performed in the presence of several heteropoly acids or their salts, and some other common or solid acids, with this oxidant under solventfree conditions (Table 1). The results show that in the absence of the catalysts, the oxidation reaction did not proceed after 30 minutes at room temperature, but in the presence of heteropoly acids this conversion proceeded efficiently in a few minutes under similar reaction conditions (Table 1, entries 2–6). In order to show the strong catalytic activity of heteropoly acids with the other acid catalysts, we have studied the catalytic activities of Amberlyst-15, Montmorillonite-K10 Clay, HY-zeolite, sulfuric acid, *p*-toluenesulfonic acid, and triflic acid for this purpose. We found that none of them was an effective catalyst for the oxidation of benzyl alcohol to benzaldehyde in the presence of ferric nitrate nonahydrate (Table 1, entries 9–14). Therefore, we chose tungstophosphoric acid; $H_3PW_{12}O_{40}$ that is a cheap and a commercially available compound as a catalyst for further oxidation studies.

Table 1 Oxidation of Benzyl Alcohol with $Fe(NO_3)_3$ ·9H2O in thePresence of Various Heteropoly Acids, their Salts and other Commonor Solid Acids at Room Temperature in a Solventless System^a

En- try	Catalyst	Subst./ Cat./ Oxidant	Time (min)	Conv. (%)	GC Yield (%) ^b
1	none	1:0:0.5	30	0	0
2	$H_3PW_{12}O_{40}$	1:0.1:0.5	4	100	>98
3	$H_3PW_{12}O_{40}{\cdot}nH_2O$	1:0.1:0.5	6	100	>98
4	$H_5 PV_2 Mo_{10}O_{40} \cdot nH_2 O$	1:0.1:0.5	5	100	>98
5	$H_4SiW_{12}O_{40}$	1:0.1:0.5	8	100	>98
6	(NH ₄) ₂ HPW ₁₂ O ₄₀	1:0.1:0.5	10	100	95
7	$\alpha \text{-} K_6 P_2 W_{18} O_{62} \text{-} 14 H_2 O$	1:0.05:0.5	30	68	43
8	$Na_2WO_4 \cdot 2H_2O$, $(CO_2H)_2$	1:1:1:0.5	30	11	11
9	amberlyst-15H+c	1:-:0.5	30	22	20
10	montmorillonite-K10 ^c	1:-:0.5	30	14	14
11	HY-Zeolite ^c	1:-:0.5	30	9	9
12	TfOH	1:0.3:0.5	30	44	35
13	TsOH	1:0.3:0.5	30	18	15
14	H_2SO_4	1:0.2:0.5	30	40	33

^a Reaction conditions: Fe(NO₃)₃·9H₂O (1 mmol), catalyst (0.05–1 mmol), benzyl alcohol (2 mmol).

^b n-Octane was used as an internal standard.

^c 0.2 g of the material was used.

Effect of Countercation

We also investigated other metal nitrates for the oxidation of benzyl alcohol to benzaldehyde under similar reaction conditions (Table 2). The results revealed that most of the metal nitrates were effective oxidants for this transformation, but iron and bismuth(III) nitrates gave better results. $Fe(NO_3)_3 \cdot 9H_2O/H_3PW_{12}O_{40}$ (with a 10:1 molar ratio) is a stable mixture and does not need any precautions that are required by Clayfen,^{12k,1} which should be prepared and used freshly and should be kept under *n*-pentane.

Table 2 Oxidation of Benzyl Alcohol with Various Metal Nitratesin the Presence of H_3PW at Room Temperature in a SolventlessSystem^a

En- try	Metal Nitrate	Subst./ H ₃ PW/ Metal Nitrate	Time (min)	Conv. (%)	GC Yield (%) ^b
1	none	1:0.1:0	30	0	0
2	NaNO ₃	1:0.1:2.5	15	16	10
3	Mg(NO ₃) ₂ ·6H ₂ O	1:0.1:1	15	47	29
4	Zn(NO ₃) ₂ ·6H ₂ O	1:0.1:1	15	50	32
5	$Cu(NO_3)_2 \cdot 3H_2O$	1:0.1:1	15	63	42
6	$Ce(NH_4)_2(NO_3)_6$	1:0.1:0.5	15	63	56°
7	$Cr(NO_3)_3 \cdot 9H_2O$	1:0.1:0.5	15	61	61
8	Bi(NO ₃) ₃ ·5H ₂ O	1:0.1:0.5	10	100	99
9	$Zr(NO_3)_4$	1:0.1:0.5	30	3	3
10	Fe(NO ₃) ₃ ·9H ₂ O	1:0.1:0.5	15	95	93 ^d
11	Fe(NO ₃) ₃ ·9H ₂ O	1:0.1:0.5	4	100	quan.
12	Fe(NO ₃) ₃ ·9H ₂ O	1:0.05:0.5	15	100	quan.

^a Reaction conditions: Metal nitrate (1 mmol), H₃PW (0.2 mmol), benzyl alcohol (2 mmol).

^b *n*-Octane was used as an internal standard.

^c We have also tried this reaction with ca. 015 equiv of

 $Ce(NH_4)_2(NO_3)_6$. Reaction proceeded under longer reaction time (ca. 2 h) with only 45% conversion to the aldehyde plus unreacted starting material.

^d Catalyst, ferric nitrate and acetone (10 mL) was mixed and stirred for 10 min. The solvent is then removed under reduced pressure at <50 °C and the obtained slurry mixture was employed for the oxidation reaction under solvent-free conditions.

Effect of Solvent

The oxidation of benzyl alcohol was also conducted in different solvents. The results show that the efficiency and the yield of the reaction in solutions were much less than that observed under solvent-free conditions (Table 3).

Therefore, we have conducted the oxidation of structurally different alcohols with this oxidation system under solvent-free conditions and the results are compared with some of those reported using Silfen, Clayfen and Zeofen (Table 4).

According to the results, our method is suitable for the oxidation of primary and secondary benzylic and secondary saturated alcohols. Allylic and propargylic alcohols afforded unidentified polymeric materials. Primary saturated alcohols were also oxidized to their aldehydes in low yields without over-oxidation to the carboxylic acids.

Table 3 Oxidation of Benzyl Alcohol with $Fe(NO_3)_3 \cdot 9H_2O$ in thePresence of Tungstophosphoric Acid (H_3PW) in Various Solvents^a

Solvent	T			
	(°C)	Time (min)	Conv. (%)	GC Yield (%)
1,2-dichloroethane	55-60	60	25	17
CHCl ₃	55-60	150	6	5
CH_2Cl_2	reflux	120	30	30
EtOAc	50	150	75	23
acetone	r.t.	15	0	0
MeCN	r.t.	150	70	39
petroleum ether	r.t.	30	100	73
<i>n</i> -hexane	r.t.	15	100	76
	1,2-dichloroethane CHCl ₃ CH ₂ Cl ₂ EtOAc acetone MeCN petroleum ether <i>n</i> -hexane	(°C) 1,2-dichloroethane 55–60 CHCl ₃ 55–60 CH2Cl ₂ reflux EtOAc 50 acetone r.t. MeCN r.t. petroleum ether r.t. n-hexane r.t.	(°C) (min) 1,2-dichloroethane 55–60 60 CHCl ₃ 55–60 150 CH ₂ Cl ₂ reflux 120 EtOAc 50 150 acetone r.t. 15 MeCN r.t. 30 petroleum ether r.t. 15	(°C) (min) (%) 1,2-dichloroethane 55-60 60 25 CHCl ₃ 55-60 150 6 CH ₂ Cl ₂ reflux 120 30 EtOAc 50 150 75 acetone r.t. 150 70 MeCN r.t. 30 100 n-hexane r.t. 15 100

^a Reaction conditions: benzyl alcohol (2 mmol), ferric nitrate

(1 mmol), H_3PW (0.2 mmol), solvent (10 mL).

Selectivity

In order to show the chemoselectivity of the method for the oxidation of different hydroxyl groups, we have performed a number of competitive reactions as shown in Scheme 1.

In conclusion, we have introduced a new catalyst for the activation of ferric nitrate nonahydrate for the oxidation of primary and secondary saturated and benzylic alcohols into their corresponding carbonyl compounds. Over-oxidation did not occur by using this method. The handling of the mixture of ferric nitrate nonahydrate and tungstophosphoric acid is easy and does not require any precaution for its storage. Stability of the oxidation system, high reaction rates, high yields of the products, solvent-free and mild reaction conditions are worthy of mention as advantages of the presented protocol.

Entry	Alcohol	Subst./H ₃ PW/ Fe(NO ₃) ₃	Product	Time (min)	Temp. (°C)	Yield ^a (%)	Yield (%) (other methods)
1	PhCH ₂ OH	1:0.1:0.5	PhCHO	5	r.t.	95	(75), ^b (81), ^c (90) ^d
2	PhCH ₂ OH	1:0.05:0.5	PhCHO	15	r.t.	96	_
3	4-MeOC ₆ H ₄ CH ₂ OH	1:0.1:0.5	4-MeOC ₆ H ₄ CHO	10	r.t.	97	(66) ^b
4	4-MeC ₆ H ₄ CH ₂ OH	1:0.1:0.5	4-MeC ₆ H ₄ CHO	10	r.t.	96	(88) ^d
5	4-ClC ₆ H ₄ CH ₂ OH	1:0.1:0.5	4-ClC ₆ H ₄ CHO	20	r.t.	97	-
6	2-NO ₂ C ₆ H ₄ CH ₂ OH	1:0.1:0.625	2-NO ₂ C ₆ H ₄ CHO	15	55-60	95	(73), ^b (85) ^d
7	2-HOC ₆ H ₄ CH ₂ OH	1:0.1:0.5	2-HOC ₆ H ₄ CHO	10	r.t.	23	_
8	Ph ₂ CHOH	1:0.1:0.625	Ph ₂ CO	15	55-60	96	(88), ^c (82) ^d
9	PhCH(OH)Me	1:0.1:0.5	PhC(O)Me	5	r.t.	95	(45), ^b (81), ^c (80) ^d
10	PhCH(OH)Et	1:0.1:0.5	PhC(O)Et	10	r.t.	94	-
11	D-PhCH(OH)CO ₂ H	1:0.1:0.75	PhC(O)CO ₂ H	10	55-60	93	_
12	PhCH(OH)C(O)Ph	1:0.1:1	PhC(O)C(O)Ph	60	55-60	95 ^e	_
13	PhCH ₂ CH ₂ OH	1:0.1:0.625	PhCH ₂ CHO	90	r.t.	60 ^f	(63) ^b
14	PhCH ₂ CH ₂ CH ₂ OH	1:0.1:0.625	PhCH ₂ CH ₂ CHO	90	r.t.	56 ^f	_
15	Me(CH ₂) ₆ CH ₂ OH	1:0.1:0.625	Me(CH ₂) ₆ CHO	24 (h)	r.t.	10–15 ^f	_
				60	55-60	52 ^f	(60) ^b
16	Me(CH ₂) ₅ CH(OH)Me	1:0.1:0.625	Me(CH ₂) ₅ C(O)Me	3 (h)	r.t.	92	_
				15	55-60	90	_
17	norborneol	1:0.1:0.625	norcamphor	15	55-60	94	_
18	PhCH(OH)CH ₂ OH	1:0.1: 0.5	PhC(O)CH ₂ OH	10	55-60	78	_

Table 4 Oxidation of Various Alcohols with Ferric Nitrate Nonahy	drate Catalyzed By the Tungstophosphoric Acid (H ₃ PW)
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^a Yields refer to isolated pure products. The products were characterized by IR and ¹H NMR spectral data.

^b Conditions: Silfen, CHCl₃, reflux, 4–5 h.^{12a}

^c Conditions: Clayfen, *n*-pentane or *n*-hexane, reflux, 1.5–3 h.^{12j,k}

^d Conditions: Zeofen, CH₂Cl₂, r.t., 20–40 min.¹³

^e In the presence of 10 drops of EtOAc.

^f Yields were determined by ¹H NMR spectroscopy.

$\frac{PhCH_2OH}{PhCH_2CH_2OH} \xrightarrow{Fe(NO_3)_3 \cdot 9H_2O(0.5 \text{ mmol}), Cat. (0.1 \text{ mmol})}{rt., neat, 60 \text{ min}} PhCHO$ $PhCH_2CH_2OH$	98% 96%
PhCH ₂ OH Me(CH ₂) ₆ CH ₂ OH $\frac{Fe(NO_3)_3 \cdot 9H_2O(0.5 \text{ mmol}), \text{Cat. (0.1 mmol)}}{\text{rt., neat, 60 min}} PhCHO$ Me(CH ₂) ₆ CH ₂ OH	97% 93%
PhCH ₂ OH ($_{D}$)-PhCH(OH)CO ₂ H $\frac{Fe(NO_3)_3 \cdot 9H_2O(0.5 \text{ mmol}), \text{Cat. (0.1 mmol)}}{\text{rt., neat, 5 min}} PhCHO(_{D})-PhCH(OH)CO2H$	97% 95%
PhCH(OH)CH ₃ $\frac{Fe(NO_3)_3 \cdot 9H_2O(0.5 \text{ mmol}), \text{ Cat. (0.1 mmol})}{rt., \text{ neat, 5 min}} PhC(O)CH_3$ (D)-PhCH(OH)CO ₂ H	95% 85%
$\begin{array}{c} Me(CH_{2})_{5}CH(OH)Me \\ Me(CH_{2})_{6}CH_{2}OH \end{array} \xrightarrow{Fe(NO_{3})_{3}\cdot 9H_{2}O(0.5 \text{ mmol}), \text{ Cat. (0.1 mmol)}}_{rt., neat, 4 \text{ h}} \qquad \begin{array}{c} Me(CH_{2})_{5}C(O)Me \\ Me(CH_{2})_{6}CH_{2}OH \end{array}$	88% 90%
PhCH ₂ OH $Me(CH_2)_5CH(OH)Me \xrightarrow{Fe(NO_3)_3 \cdot 9H_2O(0.5 \text{ mmol}), Cat. (0.1 \text{ mmol})}{rt., neat, 15 \text{ min}} PhCHO Me(CH_2)_5CH(OH)Me$	87% 97%
(b)-PhCH(OH)CO ₂ H $\frac{Fe(NO_3)_3 \cdot 9H_2O(0.5 \text{ mmol}), \text{ Cat. } (0.1 \text{ mmol})}{\text{rt., neat, } 45 \text{ min}}$ (b)-PhCH(OH)CO ₂ H Me(CH ₂) ₅ C(O)Me	88% 95%

Scheme 1

Tungstophosphoric acid (H₃PW₁₂O₄₀·nH₂O) was purchased from Merck and was purified by extraction with Et₂O from an aqueous solution of the acid. After evacuation at 150-300 °C for 1-2 h under reduced pressure, pure H3PW12O40 was obtained.14 Tungstosilicic acid, H₄SiW₁₂O₄₀·nH₂O was purchased from Merck and dehydrated by evacuating at 150-300 °C. The acidic salts of heteropoly acids were prepared according to the known procedures.¹⁵ $H_5V_2Mo_{10}O_{40}$ $\cdot nH_2O$ and α - $K_6P_2W_{18}O_{62}$ $\cdot 14H_2O$ were prepared by known procedures.^{16,17} All products are known and commercially available and hence their physical data are not given. The products were purified by column chromatography or TLC on silica gel, when necessary, the purity determination of the products was accomplished by GC on a Shimadzu model GC-14A instrument or by TLC on silica gel polygram SIL G/UV 254 plates. The IR spectra were recorded on a Perkin Elmer 781 spectrophotometer. The NMR spectra were recorded on a Bruker Avance DPX 250 MHz spectrometer.

Oxidation of Alcohols with Ferric Nitrate Nonahydrate in the Presence of Tungstophosphoric Acid; General Procedure

Ferric nitrate nonahydrate (0.404–0.808 g, 1–2 mmol,) and tungstophosphoric acid (0.288–0.576 g, 0.1–0.2 mmol) were mixed together in a test-tube and was ground gently by a glass rod. Then the corresponding alcohol (2 mmol) was added and the resulting mixture was thoroughly mixed by a glass rod for the appropriate reaction time and temperature (see Table 4). After completion of the reaction (monitored by TLC or GC, and also completion of the reaction was clearly visible by discontinuation of the evolution of reddish nitrogen dioxide fumes), the test-tube was laid aside for 10–15 min in order to expel thoroughly the nitrogen dioxide fumes. The mixture was extracted repeatedly with CH_2Cl_2 (3 × 20 mL). The combined organic solutions were washed repeatedly by aq sat. solution of NaHCO₃ (2 × 5 mL) (except for entry 11, Table 4), H₂O (2 × 25 mL), and dried (Na₂SO₄). Evaporation of the solvent under reduced pressure gave the almost pure carbonyl compound. When necessary, further purification was performed by column chromatography on silica gel (70–230 mesh) or by preparative TLC (silica gel plates) using *n*-hexane–EtOAc as eluents (Table 4, entries 11, 12, 18).

Table 4, entry 6

Anal. Calcd for $C_7H_5O_3N$: C, 55.62; H, 3.31. Found: C, 55.45; H, 3.24.

Table 4, entry 12

Anal. Calcd for $C_{14}H_{10}O_2$: C, 80.00; H, 4.76. Found: C, 79.8; H, 4.78.

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References

- Hudlicky, M. Oxidations in Organic Chemistry, ACS Monograph 186; ACS: Washington DC, 1990, .
- (2) Muzart, J. Chem. Rev. 1992, 92, 113.
- (3) (a) Mancuso, A. J.; Swern, D. Synthesis 1981, 165.
 (b) Tidwell, T. T. Synthesis 1990, 857.
- (4) (a) Dess, D. B.; Martin, J. C. J. Org. Chem. 1983, 48, 4155.
 (b) Dess, D. B.; Martin, J. C. J. Am. Chem. Soc. 1991, 113, 7277.

- (5) Klein, W. J. In Organic Syntheses by Oxidation with Metal Compounds; Mijs, W. J.; De Jonge, C. R. H. I., Eds.; Plenum: New York, **1986**.
- (6) (a) Okuhara, T.; Mizuno, N.; Misono, M. *Appl. Catal.*, A 2001, 222, 63. (b) Misono, M. *Chem. Commun.* 2001, 1141.
 (c) Kozhevnikov, I. V. *Chem. Rev.* 1998, 98, 171.
 (d) Mizuno, N.; Misono, M. *Chem. Rev.* 1998, 98, 199.
 (e) Okuhara, T.; Mizuno, N.; Misono, M. *Adv. Catal.* 1996, 41, 113.
- (7) (a) Ono, Y. In *Perspective in Catalysis*; Thomas, J. M.; Zamaraev, K. I., Eds.; Blackwell: London, **1992**, 431.
 (b) Kozhevnikov, I. V. *Catal. Rev.-Sci. Eng.* **1995**, *37*, 311.
 (c) Okuhara, T.; Misuno, N.; Misono, M. *Adv. Catal.* **1996**, *41*, 113. (d) Hill, C. L.; Prosser-McCartha, C. M. *Coord. Chem. Rev.* **1995**, *143*, 407.
- (8) (a) Kozhevnikov, I. V. *Russ. Chem. Rev.* **1987**, *56*, 811.
 (b) Okuhara, T.; Hu, C.; Hashimoto, M.; Misono, M. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1186.
- (9) (a) Tiofeeva, M. N.; Dimidov, A. V.; Kozhevnikov, I. V. J. *Mol. Catal.* **1993**, *79*, 21. (b) Drago, R. S.; Dias, J. A.; Maier, T. O. J. Am. Chem. Soc. **1997**, *119*, 7702.
 (c) Okuhara, T.; Watanabe, H.; Nishimura, T.; Inumaru, K.; Misono, M. Chem. Mater. **2000**, *12*, 2230.
- (10) (a) Misono, M.; Ono, I.; Koyano, G.; Aoshima, A. Pure Appl. Chem. 2000, 72, 1305. (b) Misono, M. C. R. Acad. Sci. Paris, Ser. IIc, Chim. 2000, 471.
- (11) (a) Firouzabadi, H.; Iranpoor, N.; Amani, K. *Green Chem.* 2000, *3*, 131. (b) Firouzabadi, H.; Iranpoor, N.; Amani, K. *Synthesis* 2001, 59. (c) Firouzabadi, H.; Iranpoor, N.; Amani, K. *J. Mol. Catal.* 2002, in print. (d) Firouzabadi, H.; Iranpoor, N.; Amani, K.; Nowrouzi, F. *J. Chem. Soc., Perkin Trans. 1* 2002, 2601.

- (12) (a) Hirano, M.; Ukawa, K.; Yakabe, S.; Morimoto, T. Synth. Commun. 1997, 27, 1527. (b) Hirano, M.; Komiya, K.; Yakabe, S.; Clark, J. H.; Morimoto, T. Org. Prep. Proced. Int. 1996, 28, 705. (c) Hirano, M.; Ukawa, K.; Yakabe, S.; Morimoto, T. Org. Prep. Proced. Int. 1997, 29, 480.
 (d) Khadilkar, B.; Borkar, S. Synth. Commun. 1998, 28, 207.
 (e) Hirano, M.; Komiya, K.; Morimito, T. Org. Prep. Proced. Int. 1995, 27, 703. (f) Cseri, T.; Bekassy, S.; Figueras, F. Bull. Soc. Chim. Fr. 1996, 133, 547.
 (g) Figueras, F.; Bekassy, S.; Cseri, T. New J. Chem. 1996, 20, 357. (h) Heravi, M. M.; Ajami, D.; Mojtahedi, M. M.; Ghassemzadeh, M. Tetrahedron Lett. 1999, 40, 561.
 (i) Varma, R. S.; Dahiya, R. Tetrahedron Lett. 1998, 39, 1307. (j) Laszlo, P.; Cornelis, A. Synthesis 1985, 909.
 (k) Laszlo, P.; Cornelis, A. Synthesis 1980, 849.
- (13) Heravi, M. M.; Ajami, D.; Mojtahedi, M. M.; Ghassemzadeh, M. Chem. Commun. 1999, 833.
- (14) Misono, M.; Misono, N.; Katamura, K.; Kasai, A.; Konishi,
 Y.; Sakata, K.; Okuhara, T.; Yoneda, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 400.
- (15) Misono, M.; Okuhara, T.; Nishimura, T.; Watanabe, H. J. Mol. Catal. **1992**, 74, 247.
- (16) Tsigdinos, G. A.; Hallada, C. J. Inorg. Chem. 1968, 7, 437.
- (17) Lyon, D. K.; Miller, W. K.; Novet, T.; Domaille, P. J.; Evitt,
 E.; Johnson, D. C.; Finke, R. G. J. Am. Chem. Soc. 1991, 113, 7209.