Available online at www.sciencedirect.com

SCIENCE DIRECT

Tetrahedron Letters

Tetrahedron Letters 46 (2005) 8483–8486

Photocatalytic oxidation of primary and secondary benzylic alcohols to carbonyl compounds catalyzed by $H_3PW_{12}O_{40}/SiO_2$ under an O_2 atmosphere

Saeid Farhadi,* Mozhgan Afshari, Mansoureh Maleki and Zaynab Babazadeh

Department of Chemistry, University of Lorestan, Khoramabad 68135-465, Iran

Received 16 August 2005; revised 29 September 2005; accepted 6 October 2005
Available online 25 October 2005

Abstract—An efficient, selective and green procedure for the photocatalytic oxidation of primary and secondary benzylic alcohols to the corresponding aldehydes and ketones has been achieved using silica-encapsulated $H_3PW_{12}O_{40}$ as a recyclable heterogeneous photocatalyst in acetonitrile under oxygen gas as the sole reoxidant of the catalyst.

The catalytic oxidation of alcohols to their corresponding carbonyl compounds using O_2 or air is of interest for both economic and environmental reasons.[1] Many thermal catalytic systems, for example, M^{II}-radical catalysts,[2] CuCl.Phen,[3] $H_5PV_2Mo_{10}O_{40}$,[4] PdL_n,[5] M-TEMPO,[6] Ru-biomimetic-coupled systems,[7] bimetallic Os–Cu and Mo–Cu systems,[8] RuO_2 and perruthenate-based catalysts,[9] Pt and Pt/Bi catalysts,[10] manganese oxide molecular sieves,[11] Ru-hydroxyapatite,[12] $RuCl_2(p\text{-cymene})_2/Cs_2CO_3$[13] and V_2O_5[14] have been designed and developed for the oxidation of alcohols by molecular oxygen. Most of these systems are particularly effective for activated (benzylic and allylic) alcohols. However, the search for suitable green aerobic catalysts is still a significant challenge. In this context, photoreactions are promising processes[15] and the development of photocatalysts is a subject that is now receiving much attention. TiO_2, which catalyzes the oxidation of various organic compounds, is one example of a practical and useful photocatalyst.[16]

An important class of photocatalysts that has received more attention in recent years is the polyoxometalates (POMs).[17] Mechanistic aspects of photocatalysis by these non-toxic compounds are well known.[18] Briefly, near UV–vis irradiation of a POM solution results in an O to M (M = W and Mo) charge-transfer excited state which has strong oxidation ability and is responsible for the oxidation of organic substrates, photoexcited POMs being reduced by the transfer of one or two electron(s) from the organic substrate. Reoxidation (regeneration) of the photoreduced POMs back to their original oxidation state can easily be affected by oxygen and this reaction is the basis for their photocatalytic activity.[19]

Most POMs are highly soluble in polar solvents and suffer from an inability to be recycled. Recently, progress has been made in the preparation of desolubilized POMs creating heterogeneous photocatalysts by encapsulating the POM molecules into a silica matrix via a sol–gel process.[20]

However, these reported studies have focused mainly on the application of these heterogeneous systems for photodegradation and mineralization of organic pollutants.[21] As far as we know, there is only one report on the application of heterogenized POMs as photocatalysts for synthetic purposes.[22]

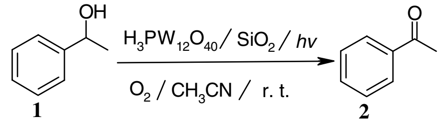
In this letter, we report a novel method for the oxidation of benzylic alcohols using sol–gel silica-encapsulated $H_3PW_{12}O_{40}$ as a heterogeneous photocatalyst. The reaction takes place under an O_2 atmosphere, which acts as a stoichiometric catalyst reoxidant thereby allowing recycling and reuse of $H_3PW_{12}O_{40}$. $H_3PW_{12}O_{40}/SiO_2$ was

---

Keywords: Benzylic alcohols; Photocatalytic; Oxidation; Polyoxometalates; Silica-encapsulated; $H_3PW_{12}O_{40}$.

* Corresponding author. Fax: +98 6614600088; e-mail: sfarhad2001@yahoo.com

0040-4039/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2005.10.019



Scheme 1.

prepared according to the reported method by a sol–gel process.[23]

Our investigation began with 1-phenylethanol (**1**) as a model substrate to check the catalytic activity of $H_3PW_{12}O_{40}/SiO_2$ for the oxidation of alcohols and to optimize the reaction conditions. We observed that when a heterogeneous mixture of this alcohol and $H_3PW_{12}O_{40}/SiO_2$ in acetonitrile was irradiated under an O_2 atmosphere, acetophenone (**2**) was formed as the only product in 84% yield within 2 h at room temperature (Scheme 1).

On the other hand, **1** was oxidized to **2** in a 75% yield within 2.75 h when pure $H_3PW_{12}O_{40}$ was used as the homogeneous photocatalyst under the same reaction conditions. This result clearly indicated that silica-encapsulated $H_3PW_{12}O_{40}$ is more active than the bulk $H_3PW_{12}O_{40}$. The significantly higher activity of the $H_3PW_{12}O_{40}/SiO_2$ composite, as compared with that of pure $H_3PW_{12}O_{40}$, is attributed to the much higher specific surface area of $H_3PW_{12}O_{40}/SiO_2$.[20c] Using a pure SiO_2 support as a catalyst, no oxidation product **2** was detected by GC analysis after 4 h irradiation, suggesting that the photocatalytic activity of $H_3PW_{12}O_{40}/SiO_2$ is derived from the encapsulated $H_3PW_{12}O_{40}$ rather than the SiO_2 support.

Leaching was shown not to occur with $H_3PW_{12}O_{40}/SiO_2$ under the conditions employed. Thus, oxidation of **1** was allowed to proceed to 50% completion, and the solid photocatalyst was removed by simple filtration; the filtrate was then irradiated at rt under an oxygen atmosphere and no further oxidation was observed by GC even after 4 h. On the other hand, to demonstrate the recyclability of the catalyst, the recovered catalyst was reused several times for further reaction runs without a significant decrease in yield or rate. Even after eight runs, 80% of pure **2** was isolated. The oxidation of **1** to **2**, did not take place when light and or O_2 were eliminated from the system. Therefore, it was confirmed that $H_3PW_{12}O_{40}/SiO_2$, light and O_2 were essential for this reaction.

These conditions were next applied to a variety of ring-substituted primary and secondary benzylic alcohols. The results are summarized in Table 1.

The reactions of primary benzylic alcohols using this procedure were clean and all the alcohols were converted into the corresponding aldehydes in moderate to excellent yields without over-oxidation to carboxylic acids (entries 1–15). An interesting electronic effect seemed to exist for these benzylic systems. Comparing benzyl alcohol (entry 1) with the benzylic alcohols containing electron-releasing substituents (e.g., entries 2–7), it was found that the reaction times for the electron-rich arenes were significantly shorter. Primary benzylic systems with electron-withdrawing groups (entries 12–14) required longer reaction times and gave lower yields. Most of the reactions of these substrates did not go to completion and increasing the irradiation time did not improve the yields.

Secondary benzylic substrates generally gave very clean, high-yielding reactions (entries 16–27). In some cases, the rate enhancement was substantial. For example, the oxidation of 1-(*p*-methylphenyl)ethanol (entry 17) was almost complete after 1 h. The electronic effect observed for primary benzylic systems also seemed to be prevalent in the case of secondary benzylic systems. 1-(*p*-Nitrophenyl)ethanol (entry 18) required a longer reaction time and gave a decreased yield when compared to more electron-rich secondary benzylic substrates.

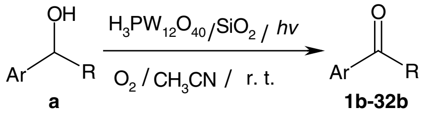
Furthermore, pyridine-4-methanol and thiophene-2-methanol were converted to the corresponding aldehydes in 74% and 78% yields, respectively, without oxidation of the N or S heteroatoms on 4 h irradiation under our reaction conditions. This reaction is also efficient for allylic systems. For example, cinnamyl alcohol gave cinnamaldehyde in a 78% yield after 2 h irradiation.

In contrast to primary and secondary benzylic alcohols and allylic alcohols which were oxidized in a highly efficient way, aliphatic and aryl-substituted non-benzylic alcohols such as 2-propanol and 3-phenyl-1-propanol were less reactive and gave the corresponding carbonyl compounds in only 15% and 18% GC yields, respectively, after very long irradiation times (10 h). Moreover, when a mixture of 1-phenylethanol and 2-phenylethanol was irradiated in the presence of $H_3PW_{12}O_{40}/SiO_2$ under O_2, the former was oxidized to acetophenone in an 85% GC yield and the latter gave 2-phenylacetaldehyde in <5% GC yield after 2 h. These findings prompted us to oxidize 1,2-diols containing benzylic and non-benzylic hydroxyl groups (entries 28–32). It was observed that these diols were cleanly oxidized to α-ketols without cleavage of the 1,2-diol bond.

While all the reactions were run on a 1 mmol scale, these oxidation conditions also proved successful on a larger scale. A 10 mmol reaction of 2,4-dimethoxybenzyl alcohol using the present procedure provided the corresponding aldehyde in an 85% isolated yield whilst a 100 mmol reaction of benzhydrol gave benzophenone in an 82% isolated yield.

In conclusion, a novel and efficient procedure for the oxidation of primary and secondary benzylic alcohols has been developed using $H_3PW_{12}O_{40}/SiO_2$ as a green and recyclable photocatalyst, under O_2 gas as the sole catalyst reoxidant. These conditions have been applied to a wide variety of substrates producing the desired carbonyl compounds in moderate to excellent yields. This reaction is highly selective for *vic*-diols in oxidizing only the secondary hydroxyl group α to the benzene ring. The

Table 1. Photocatalytic oxidation of benzylic alcohols with O_2 catalyzed by $H_3PW_{12}O_{40}/SiO_2$



Entry	Ar	R	Product[a]	Irradiation time/h	Yield/%[b]
1	C_6H_5	H	**1b**	2.5	75
2	p-MeC_6H_4	H	**2b**	1	92
3	o-MeC_6H_4	H	**3b**	1	90
4	p-$Pr^iC_6H_4$	H	**4b**	1	85
5	p-$Bu^tC_6H_4$	H	**5b**	1.5	82
6	p-$MeOC_6H_4$	H	**6b**	1.5	85
7	2,4-$(MeO)_2C_6H_3$	H	**7b**	1	88
8	o-$MeOC_6H_4$	H	**8b**	2	70
9	p-ClC_6H_4	H	**9b**	1.5	80
10	2,4-$Cl_2C_6H_3$	H	**10b**	2	85
11	p-BrC_6H_4	H	**11b**	2	82
12	p-PhC_6H_4	H	**12b**	4.5	52
13	p-$CF_3C_6H_4$	H	**13b**	4.5	50
14	p-$NO_2C_6H_4$	H	**14b**	3.5	50
15	1-$C_{10}H_7$[c]	H	**15b**	2.5	76
16	C_6H_5	CH_3	**16b**	2	84
17	p-MeC_6H_4	CH_3	**17b**	1	97
18	p-$NO_2C_6H_4$	CH_3	**18b**	3	76
19	C_6H_5	C_2H_5	**19b**	1.5	90
20	C_6H_5	n-C_3H_7	**20b**	1.5	88
21	C_6H_5	*cyclo*-C_3H_5	**21b**	1.5	90
22	C_6H_5	C_6H_5	**22b**	2	84
23	p-ClC_6H_4	C_6H_5	**23b**	1.5	88
24	p-$MeOC_6H_4$	C_6H_5	**24b**	1.25	90
25	p-$MeOC_6H_4$	p-$MeOC_6H_4$	**25b**	1	90
26	p-$NO_2C_6H_4$	C_6H_5	**26b**	3	72
27[d]	C_6H_5	$C_6H_5C{=}O$	**27b**	2.25	70
28	C_6H_5	$-CH_2OH$	**28b**	2	75
29	p-MeC_6H_4	$-CH_2OH$	**29b**	1	88
30	p-$MeOC_6H_4$	$-CH_2OH$	**30b**	1	90
31	p-ClC_6H_4	$-CH_2OH$	**31b**	1.5	84
32	p-$NO_2C_6H_4$	$-CH_2OH$	**32b**	4	68

[a] Product identification was accomplished by comparison of the physical and spectral data (TLC, mp, IR, ^{1}H NMR and MS) of the products with those of the known compounds.

[b] Yields are for isolated and chromatographically pure products.

[c] 1-Naphthyl.

[d] Benzoin.

reaction has been shown to be effective on a 100 mmol scale with no change in reactivity or yield. Work on the application of this heterogenized POM and also other heterogenized POMs for aerobic photocatalytic oxidation of various organic substrates is now in progress in our laboratory.

General procedure for the oxidation of benzylic alcohols: A solution of the benzylic alcohol (1 mmol) in acetonitrile (25 mL) was added to a Pyrex flask containing a teflon-coated stirring bar. To this solution was added $H_3PW_{12}O_{40}/SiO_2$ (0.25 g, 20 wt % of $H_3PW_{12}O_{40}$). Oxygen was passed through and the reaction mixture was kept under an oxygen atmosphere (O_2 balloon). The suspension was vigorously stirred and irradiated with a high pressure 400 W mercury lamp using a cut-off Pyrex filter at room temperature. The reaction was followed by TLC and/or GC and after an appropriate irradiation time, as shown in Table 1, the photocatalyst was filtered off. After removal of the solvent, the products were purified on a silica-gel plate or by column chromatography. Yields are shown in Table 1. All of the products were characterized by MS, IR and ^{1}H NMR, and by comparison with known compounds.[24]

Acknowledgements

Support for this research by the University of Lorestan is acknowledged.

References and notes

1. (a) Sheldon, R. A.; Arends, I. W. C. E.; Dijksman, A. *Catal. Today* **2000**, *57*, 157–166; (b) Sheldon, R. A.; Arends, I. W. C. E.; ten Brink, G.-J.; Dijksman, A. *Acc. Chem. Res.* **2002**, *35*, 774–781.
2. (a) Chaudhuri, P.; Hess, M.; Muller, J.; Hildenbrand, K.; Bill, E.; Weyhermuller, T.; Wieghardt, K. *J. Am. Chem.*

Soc. **1999**, *121*, 9599–9610; (b) Chaudhuri, P.; Hess, M.; Muller, J.; Hildenbrand, K.; Bill, E.; Weyhermuller, T.; Wieghardt, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 1095–1098.

3. Marko, I. E.; Giles, P. R.; Tsukazaki, M.; Chelle-Regnaut, I.; Gautier, A.; Brown, S. M.; Urch, C. J. *J. Org. Chem.* **1999**, *64*, 2433–2439.
4. (a) Haimov, A.; Neumann, R. *Chem. Commun.* **2002**, 876–877; (b) Khenkin, A. M.; Neumann, R. *J. Org. Chem.* **2002**, *67*, 7075–7079; (c) Khenkin, A. M.; Shimon, L. J. W.; Neumann, R. *Eur. J. Inorg. Chem.* **2001**, 789–794.
5. (a) Peterson, K. P.; Larock, R. C. *J. Org. Chem.* **1998**, *63*, 3185–3189; (b) Stahl, S. S.; Thorman, J. L.; Nelson, R. C.; Kozee, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 7188–7189; (c) Steinhoff, B. A.; Fix, S. R.; Stahl, S. S. *J. Am. Chem. Soc.* **2002**, *124*, 766–767.
6. (a) Betzemeier, B.; Cavazzini, M.; Quici, S.; Knochel, P. *Tetrahedron Lett.* **2000**, *41*, 4343–4346; (b) Dijksman, A.; Marino-Gonzalez, A.; Payeras, A. M. I.; Arends, I. W. C. E.; Sheldon, R. A. *J. Am. Chem. Soc.* **2001**, *123*, 6826–6833; (c) Cecchetto, A.; Fantana, F.; Minisci, F.; Recupero, F. *Tetrahedron Lett.* **2001**, *42*, 6651–6653; (d) Ansari, I.; Gree, R. *Org. Lett.* **2002**, *4*, 1507–1509; (e) Ragagnin, G.; Betmezeier, B.; Quici, S.; Knochel, P. *Tetrahedron* **2002**, *58*, 3985–3991.
7. Csjernyik, G.; Ell, A. H.; Fadini, L.; Pugin, B.; Backvall, J.-E. *J. Org. Chem.* **2002**, *67*, 1657–1662.
8. (a) Lorber, C. Y.; Smidt, S. P.; Osborn, J. A. *Eur. J. Inorg. Chem.* **2000**, 655–658; (b) Muldoon, J.; Brown, S. N. *Org. Lett.* **2002**, *4*, 1043–1045.
9. (a) Bleloch, A.; Johnson, B. F. G.; Ley, S. V.; Price, A. J.; Shephart, D. S.; Thomas, A. W. *Chem. Commun.* **1999**, 1907–1908; (b) Ji, H.-B.; Wang, L.-F. *Chin. J. Chem.* **2002**, *20*, 944–950; (c) Hasan, M.; Musawir, M.; Davey, P. N.; Kozhevnikov, I. V. *J. Mol. Catal. A: Chem.* **2002**, *180*, 77–84; (d) Ciriminna, R.; Pagliaro, M. *Chem. Eur. J.* **2003**, *9*, 5067–5073; (e) Zhan, B.-Z.; White, M. A.; Sham, T.-K.; Pincock, J. A.; Doucet, R. J.; Rao, K. V. R.; Robertson, K. N.; Cameron, T. S. *J. Am. Chem. Soc.* **2003**, *125*, 2195–2199.
10. (a) Kluytmans, J. H. J.; Markusse, A. P.; Kuster, B. F. M.; Marin, G. B.; Schouten, J. C. *Catal. Today* **2000**, *57*, 127–141; (b) Besson, M.; Gallezot, P. *Catal. Today* **2000**, *57*, 143–155; (c) Mallat, T.; Baiker, A. *Chem. Rev.* **2004**, *104*, 3037–3058.
11. Son, Y.-C.; Makwana, V. D.; Howell, A. R.; Suib, S. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 4280–4283.
12. Yamaguchi, K.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2000**, *122*, 7144–7145.
13. Lee, M.; Chang, S. *Tetrahedron Lett.* **2000**, *41*, 7507–7510.
14. Velusamy, S.; Punniyamuthy, T. *Org. Lett.* **2004**, *6*, 217–219.
15. Horspool, W. M.; Song, P. S. *CRC Handbook of Organic Photochemistry and Photobiology*; CRC Press: Boca Raton, 1995.
16. (a) Fox, M. A.; Dulay, M. T. *Chem. Rev.* **1993**, *93*, 341–357; (b) Hoffmann, M. R.; Martin, T. S.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69–96; (c) Fujishima, A.; Rao, T. N.; Tryk, D. A. *Photochem. Photobiol. C: Photochem. Rev.* **2000**, *1*, 1–21.
17. Papaconstantinou, E. *J. Chem. Soc., Chem. Commun.* **1982**, 12–13.
18. (a) Hill, C. L.; Bouchard, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 5148–5157; (b) Nomiya, K.; Sugie, Y.; Miyazaki, T.; Miwa, M. *Polyhedron* **1986**, *5*, 1267–1271; (c) Yamase, T.; Usami, T. *J. Chem. Soc., Dalton Trans.* **1988**, 183–190; (d) Papaconstantinou, E. *Chem. Soc. Rev.* **1989**, *18*, 1–31; (e) Hiskia, A.; Papaconstantinou, E. *Inorg. Chem.* **1992**, *31*, 163–167; (f) Maldotti, A.; Amadelli, R.; Varani, G.; Tollari, S.; Porta, F. *Inorg. Chem.* **1994**, *33*, 2968–2973; (g) Duncan, D. C.; Netzel, T. L.; Hill, C. L. *Inorg. Chem.* **1995**, *34*, 4640–4646; (h) Mylonas, A.; Papaconstantinou, E. *J. Photochem. Photobiol. A: Chem.* **1996**, *94*, 77–82; (i) Tanielian, C. *Coord. Chem. Rev.* **1998**, *178–180*, 1165–1181.
19. (a) Yamase, T. *Chem. Rev.* **1998**, *98*, 307–325; (b) Hiskia, A.; Mylonas, A.; Papaconstantinou, E. *Chem. Soc. Rev.* **2001**, *30*, 62–69.
20. (a) Izumi, Y.; Hisano, K.; Hida, T. *Appl. Catal. A: Gen.* **1998**, *181*, 277–282; (b) Molinari, A.; Amadelli, R.; Carassiti, V.; Maldotti, A. *Eur. J. Inorg. Chem.* **2000**, *6*, 91–96; (c) Mizuno, N.; Misono, M. *Chem. Rev.* **1998**, *98*, 199–217.
21. (a) Guo, Y.; Li, D.; Hu, C.; Wang, E.; Wang, Y.; Zhou, Y.; Feng, S. *Appl. Catal. B: Environ.* **2001**, *30*, 337–349; (b) Peng, G.; Wang, Y.; Hu, C.; Wang, E.; Feng, S.; Zhou, Y.; Ding, H.; Liu, Y. *Appl. Catal. A: Gen.* **2001**, *218*, 91–99; (c) Ozer, R. R.; Ferry, J. L. *J. Phys. Chem. B* **2002**, *106*, 4336–4342; (d) Li, D.; Guo, Y.; Hu, C.; Mao, L.; Wang, E. *Appl. Catal. A: Gen.* **2002**, *235*, 11–20; (e) Guo, Y.; Hu, C.; Jiang, S.; Guo, C.; Yang, Y.; Wang, E. *Appl. Catal. B: Environ.* **2002**, *36*, 9–17; (f) Guo, Y.; Hu, C.; Jiang, C.; Yang, Y.; Jiang, S.; Li, X.; Wang, E. *J. Catal.* **2003**, *217*, 141–151; (g) Anandan, S.; Ryu, S. Y.; Cho, W.; Yoon, M. *J. Mol. Catal. A: Chem.* **2003**, *195*, 201–208; (h) Jiang, C.; Guo, Y.; Hu, C.; Wang, C.; Li, D. *Mater. Res. Bull.* **2004**, *39*, 251–261; (i) Yang, Y.; Wu, Q.; Guo, Y.; Hu, C.; Wang, E. *J. Mol. Catal. A: Chem.* **2005**, *225*, 203–212.
22. Molinari, A.; Amadelli, R.; Andreotti, L.; Maldotti, A. *J. Chem. Soc., Dalton Trans.* **1999**, 1203–1204.
23. Guo, Y.; Wang, Y.; Hu, C.; Wang, Y.; Wang, E.; Zhou, Y.; Feng, S. *Chem. Mater.* **2000**, *12*, 3501–3508.
24. (a) Moriarty, R. M.; Hu, H.; Gupta, S. C. *Tetrahedron Lett.* **1981**, *22*, 1283–1286; (b) Sorg, G.; Mengel, A.; Jung, G.; Rademann, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 4395–4397; (c) Mulbaier, M.; Giannis, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 4393–4394; (d) Moore, J. D.; Finney, S. N. *Org. Lett.* **2002**, *4*, 3001–3003; (e) Reed, N. N.; Delgado, M.; Hereford, K.; Clapham, B.; Janda, K. D. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 2047–2049.