ORGANIC LETTERS

2007
Vol. 9, No. 8
1501−1504

Tightly Convoluted Polymeric Phosphotungstate Catalyst: An Oxidative Cyclization of Alkenols and Alkenoic Acids

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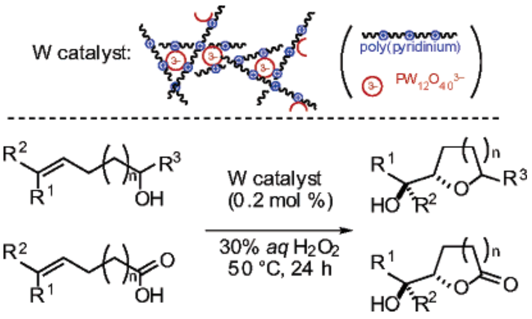
Received February 1, 2007

ABSTRACT



A tightly convoluted polymeric phosphotungstate catalyst was prepared via ionic assembly of $H_3PW_{12}O_{40}$ and poly(alkylpyridinium). An oxidative cyclization of various alkenols and alkenoic acids was efficiently promoted by the polymeric catalyst in aq H_2O_2 in the absence of organic solvents to afford the corresponding cyclic ethers and lactones in high yield. The catalyst was reused four times without loss of catalytic activity.

The development of immobilized catalysts exhibiting high aquacatalytic activity[1] and recyclability[2] has become an important topic in organic chemistry today.[3,4] We have developed amphiphilic polymer resin-supported transition-metal complexes and nanoparticles that catalyze various organic transformations in water under heterogeneous conditions.[5−7] Recently, we have also presented a novel self-assembling protocol for the preparation of solid-phase catalysts where metal species served as cross-linkers of non-cross-linked polymeric ligands as well as catalytically active centers.[8,9] Thus, for example, an ionically cross-linked polymeric phosphotungstate catalyst PWAA was prepared via salt formation of $PW_{12}O_{40}^{3-}$ with poly{{[3-(acryloylamino)propyl]dodecyldimethylammonium nitrate}-*co*-(*N*-iso-

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[3] For general reviews on green chemistry, see: (a) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford Univ. Press: Oxford, 1998. (b) *Green Chemical Syntheses and Processes: Recent Advances in Chemical Processing*; Anastas, P. T., Heine, L. G., Williamson, T. C., Ed.; Am. Chem. Soc.: Ohio, 2001. (c) Tundo, P.; Anastas, P.; Black, D. S.; Breen, J.; Collins, T.; Memoli, S.; Miyamoto, J.; Polyakoff, M.; Tumas, W. *Pure Appl. Chem.* **2000**, *72*, 1207.

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10.1021/ol070258v CCC: $37.00

propylacrylamide)$_{12}$}, a main chain of poly(*N*-isopropylacrylamide) bearing branched ammonium cation parts (Figure 1, top).[10] The polymeric phosphotungstate PWAA catalyzed the oxidation of alkenes, amines, and sulfides; however, it could not be sufficiently recycled presumably due to its physical fragility. More rigid assembling of the cationic polymer with the phosphotungstate anion might provide more stable polymeric catalysts. Here we would like to report the amphiphilic pyridinium polymer **1** bearing main-chain cationic groups constructed with a tightly convoluted pyridinium phosphotungstate salt which exhibited high catalytic activity and recyclability for oxidative cyclization of alkenols and alkenoic acids (Figure 1, bottom). The polymeric pyridinium phosphotungstate was found to catalyze the oxidative cyclization of a wide variety of (*E*)- and (*Z*)-alkenols as well as (*E*)- and (*Z*)-alkenoic acids with high stereospecificity in aqueous hydrogen peroxide under organic solvent-free conditions and was reused four times without loss of catalytic activity.

A polymeric tungsten catalyst was readily prepared from poly[1,8-dibromooctane-*co*-1,3-di(4-pyridyl)propane] (**1**)[11] with $H_3PW_{12}O_{40}$ (**2**)[12] according to the preparation of $[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3PW_{12}O_{40}$.[13] Thus, when an aqueous solution of **2** was added to an aqueous solution of **1** at 25 °C, the ionic components assembled to give the polymeric salt **3** as a white powder (83% yield), which was insoluble in water, ethanol, ethyl acetate, tetrahydrofuran, dichloromethane, toluene, and hexane (Scheme 1).[14]

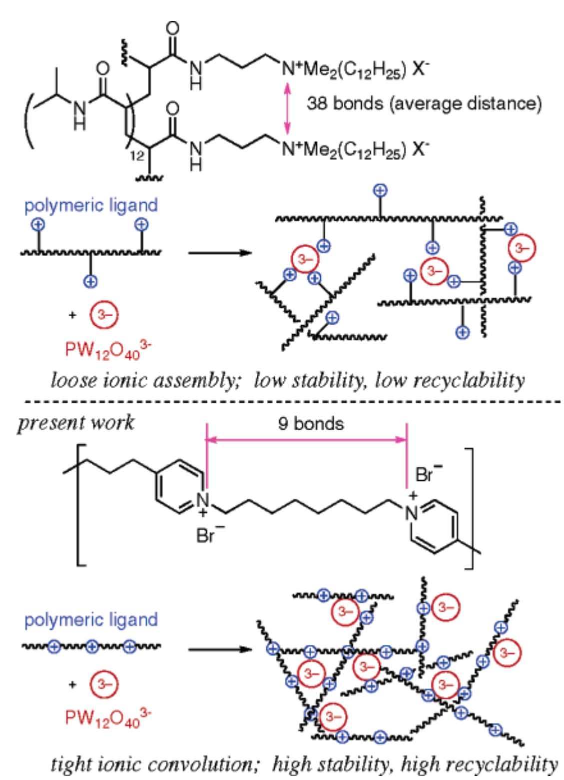

Figure 1. Assembly of $H_3PW_{12}O_{40}$ and an amphiphilic copolymer with a branched ligand (top) and a tight assembly of $H_3PW_{12}O_{40}$ and a main-chain pyridinium polymer (bottom).

The polymeric phosphotungstate **3** was unambiguously characterized by spectro- and microscopic studies (MAS ^{31}P-{^{1}H} NMR, IR spectroscopy, elemental analysis, TEM, SEM, and EDS). Typical data are shown in Figure 2. MAS ^{31}P-{^{1}H} NMR of the polymeric **3** showed a narrow singlet resonance at −16.5 ppm that was identical to a phosphorus resonance of $PW_{12}O_{40}{}^{3-}$.[15,16] High-resolution TEM analysis of **3** revealed that the phosphotungstate clusters were uniformly dispersed throughout the polymer matrix having a diameter of ca. 1 nm, which is consistent with the size of

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(5) For aquacatalytic reactions with amphiphilic resin-supported transition-metal complexes, see: (a) Uozumi, Y.; Danjo, H.; Hayashi, T. *Tetrahedron Lett.* **1997**, *38*, 3557. (b) Danjo, H.; Tanaka, D.; Hayashi, T.; Uozumi, Y. *Tetrahedron* **1999**, *55*, 14341. (c) Uozumi, Y.; Danjo, H.; Hayashi, T. *J. Org. Chem.* **1999**, *64*, 3384. (d) Uozumi, Y.; Watanabe, T. *J. Org. Chem.* **1999**, *64*, 6921. (e) Shibatomi, K.; Nakahashi, T.; Uozumi, Y. *Synlett* **2000**, 1643. (f) Uozumi, Y.; Nakai, Y. *Org. Lett.* **2002**, *4*, 2997. (g) Uozumi, Y.; Nakazono, M. *Adv. Synth. Catal.* **2002**, *344*, 274. (h) Uozumi, Y.; Kimura, T. *Synlett* **2002**, 2045. (i) Uozumi, Y.; Kobayashi, Y. *Heterocycles* **2003**, *59*, 71. (j) Nakai, Y.; Uozumi, Y. *Org. Lett.* **2005**, *7*, 291. (k) Uozumi, Y.; Kikuchi, M. *Synlett* **2005**, 1775. (l) Nakai, Y.; Kimura, T.; Uozumi, Y. *Synlett* **2006**, 3065. (m) Uozumi, Y.; Suzuka, T.; Kawade, R.; Taknaka, H. *Synlett* **2006**, 2109.

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(11) Jegal, J.; Kim, J.-H.; Park, Y.-I.; Lee, K.-H. *J. Appl. Polym. Sci.* **1994**, *54*, 65.

(12) (a) Misono, M. *Chem. Commun.* **2001**, 1141. (b) Mizuno, N.; Misono, M. *Chem. Lett.* **1987**, 967. (c) Okuhara, T. *Chem. Rev.* **2002**, *102*, 3641.

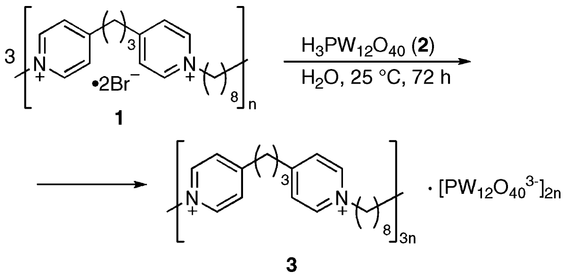
(13) Ishii, Y.; Yamawaki, K.; Ura, T.; Yamada, H.; Yoshida, T.; Ogawa, M. *J. Org. Chem.* **1988**, *53*, 3587.

(14) Preparation of **3**: To an aqueous solution (30 mL) of poly[1,8-dibromooctane-co-1,3-di(4-pyridyl)propane] (**1**) (148 mg, 0.63 mmol of a pyridinium unit) was added an aqueous solution (70 mL) of $H_3PW_{12}O_{40}$ **2** (608 mg, 0.21 mmol) at 25 °C, and the resulting colorless suspension was stirred for 3 days at the same temperature. The precipitates were collected by filtration, washed with water, and dried at 5 Pa for 12 h to give **3** (624 mg, 83%) as a colorless powder.

(15) Okuhara, T.; Watanabe, H.; Nishimura, T.; Inumaru, K.; Misono, M. *Chem. Mater.* **2000**, *12*, 2230.

(16) (a) Ishii, Y.; Tanaka, H.; Nishiyama, Y. *Chem. Lett.* **1994**, 1. (b) Massart, R.; Contant, R.; Fruchart, J.-M.; Ciabrini, J.-P.; Fournier, M. *Inorg. Chem.* **1977**, *16*, 2916.

Scheme 1. Preparation of a New-Generation Self-Assembled Polymeric Tungsten Catalyst[a]



[a] **1** (3 mol equiv of a pyridinium), **2** (1 mol equiv), water, 25 °C, 3 days.

monomeric $PW_{12}O_{40}^{3-}$.[17] The NMR and TEM observations indicate the integrity of the monomeric structure of $PW_{12}O_{40}^{3-}$, whereas a similar phosphotungstate $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is known to form an aggregated tertiary structure ($(Cs_{2.5}H_{0.5}$-$PW_{12}O_{40})_n$; $\phi = 100-500$ nm).[12] An SEM image of **3** confirmed its dendroidal surface. The polymeric phosphotungstate **3** was expected to exhibit good catalytic performance owing to the immense surface area of the convoluted composite **3** and the monomeric structure of the phosphotungstate cluster.

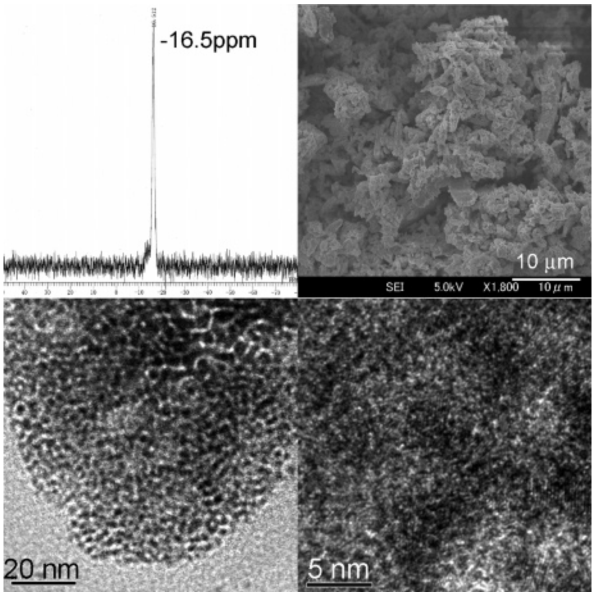
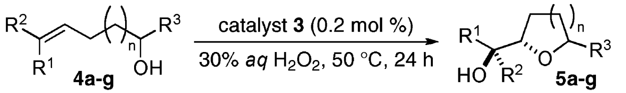
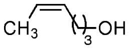
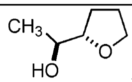
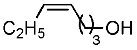
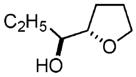
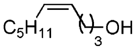
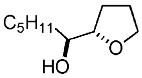
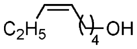
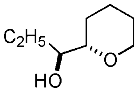
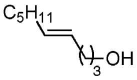
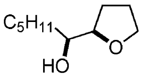
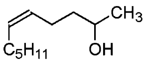
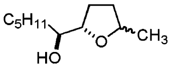
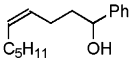
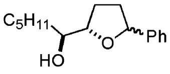


Figure 2. MAS $^{31}P\{^1H\}$ NMR (top, left), SEM (top, right; bar length = 10 μm), and TEM (bottom; left, bar length = 20 nm; right, bar length = 5 nm) images of the solid-phase catalyst **3**.

Table 1. Oxidative Cyclization of Alkenols and Alkenoic Acids Catalyzed by **3**[a]



entry	substrate	product	yield (%)
1	 **4a**	 **5a**	96
2	 **4b**	 **5b**	98
3	 **4c**	 **5c**	92
4	(2nd use)		99
5	(3rd use)		99
6	(4th use)		94
7	(5th use)		99
8	(6th use)		94[b]
9	 **4d**	 **5d**	74
10[c]	 **4e**	 **5e**	82
11	 **4f**	 **5f**	86 (1:1)[d]
12	 **4g**	 **5g**	82 (1:1)[d]

[a] All reactions were performed in the presence of **4** (1 mol equiv), 30% aq H_2O_2 (2.5 mol equiv), and **3** (0.2 mol % of phosphotungstate) at 50 °C for 24 h. [b] The catalyst was reused after being stored for 6 months. [c] **3** (0.4 mol %); aq H_2O_2 (3.5 mol equiv); reaction time, 35 h. [d] Diastereomeric ratio.

The aquacatalytic potential of the novel polymeric phosphotungstate **3** was examined for the oxidative cyclization of alkenols with aqueous hydrogen peroxide (Table 1) producing furanyl and pyranyl carbinols, which are the key components of biologically active compounds.[18,19] Although only homogeneous transition-metal catalysts have been developed for oxidative cyclizations so far,[20] the development of immobilized solid-phase catalysts still remains a major

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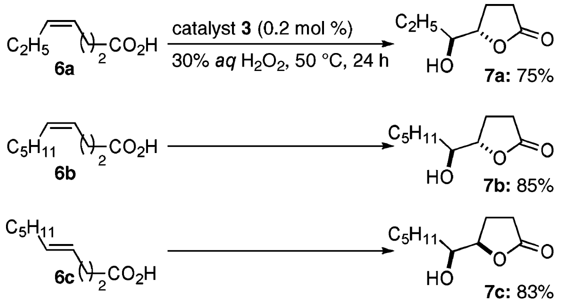
(20) For reviews, see: (a) Hartung, J.; Greb, M. *J. Organomet. Chem.* **2002**, *661*, 67. (b) Koert, U. *Synthesis* **1995**, 115. (c) Boivin, T. L. B. *Tetrahedron* **1987**, *43*, 3309. Ishii and co-authors reported one entry of the oxidative cyclization catalyzed by ($[C_5H_5N^+(CH_2)_{15}CH_3]_3\{PO_4[W(O)^-(O_2)_2]_4\}^{3-}$), where the 5-exo/6-endo cyclization selectivity was 2:1. See: (d) Sakaguchi, S.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem*. **1996**, *61*, 5307.

challenge in terms of catalytic activity and recyclability.[21] When the oxidations of the *cis*-alkenols, (*Z*)-4-hexen-1-ol (**4a**), (*Z*)-4-hepten-1-ol (**4b**), and (*Z*)-4-decen-1-ol (**4c**), were carried out with **3** (0.2 mol % of $PW_{12}O_{40}^{3-}$) in 30% aqueous H_2O_2 at 50 °C, we were pleased to find that the *threo*-1-(2-tetrahydrofuranyl)alkanols **5a**−**c** were obtained in 92−98% yield with complete diastereoselectivity (entries 1−3). The cyclization of (*Z*)-5-octen-1-ol (**4d**) proceeded smoothly to give the *threo*-tetrahydropyranyl alcohol **5d** in 74% yield (entry 9). (*E*)-4-Decen-1-ol (**4e**) also underwent the cyclization to give the *erythro*-product **5e** in 82% yield (entry 10). These stereochemical observations indicate that the cyclization involves a stereospecific reaction pathway. The secondary alcohols **4f** and **4g** were converted to the corresponding *threo*-tetrahydrofuranols **5f** and **5g** in 86% and 82% yield, respectively, without control of the stereochemistry at the C5-position of the tetrahydrofuran (entries 11 and 12).[22]

Recycling experiments of the insoluble catalyst **3** were examined in the oxidative cyclization of **4c** (entries 3−7). Thus, the first use of the catalyst afforded **5c** in 92% yield. After being recovered by filtration, washed with water, and dried in vacuo, the catalyst was reused to give **5c** in quantitative yield. To our delight, the third, fourth, and fifth uses of the recovered catalyst also provided **5c** in 99%, 94%, and 99% yields, respectively. After the fifth use (entry 7), the recovered catalyst was stored for 6 months under atmospheric conditions at ambient temperature and then subjected to the sixth run (entry 8) to give 94% yield of **5c**.

Alkenoic acids were also suitable substrates for the oxidative cyclization (Scheme 2). Thus, the oxidative cyclization of (*Z*)-4-heptenoic acid (**6a**), (*Z*)-**6b**, and (*E*)-4-decenoic acid **6c** under similar conditions proceeded stereospecifically to afford the corresponding lactones **7a**−**c** in 75−85% yield. By using this catalytic system, L-factor (leucomycin-inducing factor) **7b**, isolated from *Streptomyces griseus*,[23] was obtained in 85% yield.

Scheme 2



In conclusion, the novel tightly convoluted polymeric phosphotungstate cluster catalyst **3** was readily prepared via the ionic self-assembly process of a main-chain polypyridinium and phosphotungstic acid. It is noteworthy that this polymeric catalyst effectively catalyzed the oxidative cyclization of a variety of alkenols and alkenoic acids in aqueous H_2O_2 under organic solvent-free conditions. The insoluble catalyst was reused without any loss of catalytic activity. Extension of this catalytic system to other organic transformations as well as its application to the synthesis of natural products are currently in progress.

Acknowledgment. This work was supported by the CREST program, sponsored by the JST. We also thank the JSPS (Grant-in-Aid for Scientific Research, no. 15205015 and no. 16790025) and the MEXT (Scientific Research on Priority Areas, no. 460) for partial financial support of this work. We are thankful to Dr. Satoru Nakao (IMS) for his help in measuring SEM, which is supported by the Nanotechnology Support Project (MEXT) and managed by the IMS.

Supporting Information Available: Experimental details, as well as NMR, SEM, and GC-MS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) For recent examples of development, see: (a) Bhaumik, A.; Tatsumi, T. *J. Catal.* **2000**, *189*, 31. (b) Ichihara, J.; Kambara, A.; Iteya, K.; Sugimoto, E.; Shinkawa, T.; Takaoka, A.; Yamaguchi, S.; Sasaki, Y. *Green Chem.* **2003**, *5*, 491.

(22) According to Mizuno and Misono's studies (ref 12), we speculate the reaction pathway of the present oxidative cyclization should proceed via the epoxidation of the alkene (**4** or **6**) with peroxotungstate generated in situ and subsequent oxirane ring opening with the intramolecular oxygen nucleophile to afford the product (**5** or **7**).

(23) Grafe, U.; Eritt, I. *J. Antibiot.* **1983**, *36*, 1592.