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Wacker-type oxidation of cyclopentene under dioxygen atmosphere catalyzed by Pd(OAc)₂/NPMoV on activated carbon

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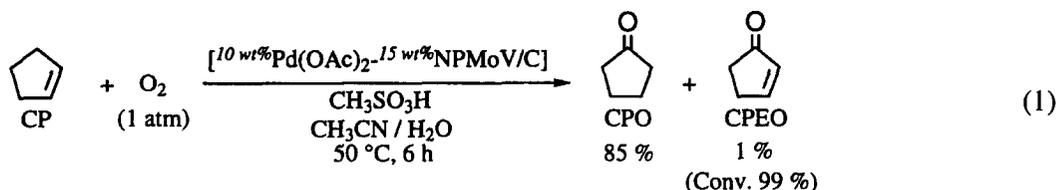
Abstract

Wacker-type oxidation of cyclopentene to cyclopentanone under dioxygen atmosphere was successfully achieved by the use of Pd(OAc)₂ and molybdovanadophosphate supported on activated carbon, [Pd(OAc)₂-NPMoV/C], catalyst. Thus, the reaction of cyclopentene under O₂ (1 atm) in aqueous acetonitrile acidified by CH₃SO₃H in the presence of [Pd(OAc)₂-NPMoV/C] at 50°C produced cyclopentanone in 85% yield along with a small amount of cyclopentenone (1%). © 1999 Elsevier Science Ltd. All rights reserved.

The oxidation of terminal alkenes by the Wacker system consisting of PdCl₂/CuCl₂/O₂ to form the corresponding ketones is a well-established method and a very important process in both synthetic and industrial chemistry.¹ However, this catalytic system has disadvantages caused by the chlorine anion which leads to the formation of chlorinated by-products and corrodes the reactor, and it is not suitable for oxidation of higher olefins and cycloalkenes.² For this reason much effort has been devoted to the development of aerobic oxidation of cycloalkenes using chloride-free oxidizing systems.³ Heteropolyacids have frequently been used as the reoxidation catalyst of the reduced Pd(0) to Pd(II) in place of CuCl₂.⁴

Cyclopentanone (CPO) is an important starting material for the synthesis of a variety of pharmaceuticals and perfumes involving a cyclopentanone framework as exemplified by jasmonates. Although there have been several reports on the synthesis of CPO from cyclopentene (CP) by the Wacker system,⁵ CPO is currently manufactured by the Dieckmann condensation of adipic acid. Therefore, if CPO can be produced by a chloride-free Wacker-type oxidation of CP, this method would provide a very useful means for the synthesis of CPO, because CP is easily obtained by partial hydrogenation of cyclopentadiene which is a very cheap compound and easily available from the petroleum industry.

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We would like to report here heterogeneous Wacker-type oxidation of CP to CPO by Pd(II) and molybdovanadophosphate (NPMoV) supported on activated carbon (hereafter abbreviated to Pd(II)-NPMoV/C)⁶ using molecular oxygen as the terminal oxidant (Eq. (1)).

A typical reaction was carried out as follows: To a suspended solution of [10 wt%Pd(OAc)₂-15 wt%NPMoV/C] (100 mg) was added CP (2 mmol) and CH₃SO₃H (20 mg), and the mixture was stirred under dioxygen atmosphere (1 atm) at 50°C for 6 h (standard conditions). Products were isolated by column chromatography on silica gel with hexane:ethyl acetate (10:1) eluent.

Table 1 shows the representative results for the oxidation of CP to CPO by [10 wt%Pd(OAc)₂-15 wt%NPMoV/C] under various conditions. The oxidation of CP by [10 wt%Pd(OAc)₂-15 wt%NPMoV/C] in acidic CH₃CN/H₂O under the standard conditions afforded CPO in 85% yield along with a small amount of cyclopentenone (CPEO) (1%) (run 1). The oxidation was markedly affected by the acid-

Table 1
Oxidation of cyclopentene (CP) to cyclopentanone (CPO) and cyclopentenone (CPEO) under various reaction conditions^{a)}

Run	Solvent	Conv. / %	Yield / %	
			CPO	CPEO
1	CH ₃ CN	99	85	1
2 ^{b)}	CH ₃ CN	>99	75	1
3 ^{c)}	CH ₃ CN	no reaction		
4 ^{d)}	CH ₃ CN	37	7	—
5 ^{e)}	CH ₃ CN	84	58	—
6 ^{f)}	CH ₃ CN	>99	68	1
7 ^{g)}	CH ₃ CN	13	8	—
8 ^{h)}	CH ₃ CN	5	2	—
9 ⁱ⁾	CH ₃ CN	>99	75	1
10 ^{j)}	CH ₃ CN	26	2	—
11	EtOH	94	66	6
12 ^{k)}	EtOH	83	55	6
13 ^{l)}	EtOH	99	75	6
14 ^{m)}	CH ₃ CN	31	3	—
15 ⁿ⁾	EtOH	95	90	4

a) CP (2 mmol) was allowed to react with O₂ (1atm) in the presence of catalyst (100 mg) and CH₃SO₃H (20 mg) in solvent / H₂O (4.5 / 0.5 mL) at 50 °C for 6 h. b) *p*-Toluenesulfonic acid (38 mg) was used instead of CH₃SO₃H. c) In the absence of CH₃SO₃H. d) Activated carbon was Darco. e) Activated carbon was Shirasagi. f) Activated carbon was Kurare coal GLC. g) [10 wt%PdCl₂-15 wt%NPMoV/C] was used. h) [10 wt%Pd(SO₄)₂-15 wt%NPMoV/C] was used. i) Pd(OAc)₂ (10 mg) and NPMoV (15 mg) was used instead of [10 wt%Pd(OAc)₂-15 wt%NPMoV/C]. j) Recovered catalyst from run 1 was used. k) Recovered catalyst from run 11 was used. l) NPMoV (15mg) was added to the recovered catalyst from EtOH / H₂O (4.5 / 0.5 mL). m) NPMoV (15mg) was added to the recovered catalyst from CH₃CN / H₂O (4.5 / 0.5 mL). n) The reaction was performed using [10 wt%Pd(OAc)₂/C] (100 mg) and NPMoV (15 mg) in EtOH / H₂O (4.5 / 0.5 mL) at 50 °C for 2 h.

ity of the reaction medium. Although *p*-toluenesulfonic acid had the same effect as $\text{CH}_3\text{SO}_3\text{H}$, the reaction in the absence of acid resulted in no formation of CPO (runs 2 and 3). Similar rate enhancement by the addition of acid is reported by several authors.⁸ In a previous paper, we showed that the aerobic oxidation of benzyl alcohols by NPMoV/C is facilitated by adding an acid, and that the reoxidation of the reduced $[\text{NPMoV}]_{\text{red}}$ to the original oxidation state of NPMoV proceeds smoothly under acidic conditions.⁹ Thus, CP was converted into CPO in satisfactory yield in acidic $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ under the influence of $[\text{}^{10}\text{ wt}\% \text{Pd}(\text{OAc})_2 - 15\text{ wt}\% \text{NPMoV}/\text{C}]$. Among the activated carbons used, Kurare BP-25 was the best support (runs 4 to 6). $\text{Pd}(\text{OAc})_2$ -NPMoV supported on activated carbon having large surface area showed higher activity. We believe that dioxygen adsorbed on the activated carbon promotes smooth reoxidation of reduced $[\text{NPMoV}]_{\text{red}}$ to NPMoV which oxidizes Pd(0) to Pd(II). Several Pd(II) catalysts, $[\text{}^{10}\text{ wt}\% \text{Pd}(\text{SO}_4)_2 - 15\text{ wt}\% \text{NPMoV}/\text{C}]$ and $[\text{}^{10}\text{ wt}\% \text{PdCl}_2 - 15\text{ wt}\% \text{NPMoV}/\text{C}]$ which were loaded on the Kurare BP-25 were prepared, and the activity of these catalysts was compared with that of the $[\text{}^{10}\text{ wt}\% \text{Pd}(\text{OAc})_2 - 15\text{ wt}\% \text{NPMoV}/\text{C}]$ (runs 7 and 8). The order of the activity of catalysts was as follows: $[\text{}^{10}\text{ wt}\% \text{Pd}(\text{OAc})_2 - 15\text{ wt}\% \text{NPMoV}/\text{C}]$, $[\text{}^{10}\text{ wt}\% \text{PdCl}_2 - 15\text{ wt}\% \text{NPMoV}/\text{C}]$ and then $[\text{}^{10}\text{ wt}\% \text{Pd}(\text{SO}_4)_2 - 15\text{ wt}\% \text{NPMoV}/\text{C}]$. It is interesting that the activity of $[\text{}^{10}\text{ wt}\% \text{Pd}(\text{OAc})_2 - 15\text{ wt}\% \text{NPMoV}/\text{C}]$ is higher than that of non-supported $\text{Pd}(\text{OAc})_2$ combined with NPMoV which gave CPO (75%) and CPEO (1%) (run 9). The benefit of the use of heterogeneous $[\text{}^{10}\text{ wt}\% \text{Pd}(\text{OAc})_2 - 15\text{ wt}\% \text{NPMoV}/\text{C}]$ is that the catalyst can be easily recovered by filtration from the reaction mixture. The oxidation of CP by the recovered $[\text{}^{10}\text{ wt}\% \text{Pd}(\text{OAc})_2 - 15\text{ wt}\% \text{NPMoV}/\text{C}]$ catalyst from aqueous CH_3CN resulted in CPO in lower yield than that by the fresh catalyst (run 10). From the ICP analysis, it was found that the deactivation of the catalyst is attributed to the leaching of metal ions ($\text{Pd}=9.03 \times 10^{-3}$ mmol (41%), $\text{Mo}=0.16 \times 10^{-3}$ mmol (1%), $\text{V}=8.64 \times 10^{-3}$ mmol (26%)) from the $[\text{}^{10}\text{ wt}\% \text{Pd}(\text{OAc})_2 - 15\text{ wt}\% \text{NPMoV}/\text{C}]$ catalyst to the aqueous CH_3CN . Although the oxidation of CP by fresh $[\text{}^{10}\text{ wt}\% \text{Pd}(\text{OAc})_2 - 15\text{ wt}\% \text{NPMoV}/\text{C}]$ in $\text{EtOH}/\text{H}_2\text{O}$ led to CPO in slightly lower yield than that in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (run 11), it was found that the leaching of the Pd ion from the catalyst was markedly suppressed. The quantity of leaching of metal ions to aqueous EtOH was as follows: $\text{Pd}=0.25 \times 10^{-3}$ mmol (1%), $\text{Mo}=0.21 \times 10^{-3}$ mmol (1%), $\text{V}=6.15 \times 10^{-3}$ mmol (18%). Therefore, when NPMoV was added to the recovered catalyst from the $\text{EtOH}/\text{H}_2\text{O}$, CPO was obtained in high yield (run 13). This indicates that the added NPMoV can reoxidize the Pd(0) species to a Pd(II) species. Thus, the oxidation by $[\text{}^{10}\text{ wt}\% \text{Pd}(\text{OAc})_2/\text{C}]$ catalyst in the presence of NPMoV was examined in $\text{EtOH}/\text{H}_2\text{O}$ at 50°C for 2 h, and CPO was obtained in high yield (90%) together with CPEO (4%) (run 15). Table 2 shows the oxidation of CP by $[\text{}^{10}\text{ wt}\% \text{Pd}(\text{OAc})_2/\text{C}]$ (100 mg) and its recovered catalyst combined with NPMoV. It is interesting to note that the catalytic activity of $[\text{}^{10}\text{ wt}\% \text{Pd}(\text{OAc})_2/\text{C}]$ was maintained after using three times.

Table 2
Oxidation of CP by the recovered catalyst^{a)}

Recovery Time	Conv. / %	Yield / %	
		CPO	CPEO
0	95	90	4
1	99	92	3
2	93	88	2
3	62	58	2

a) CP (2 mmol) was allowed to react with O_2 (1 atm) in the presence of $[\text{}^{10}\text{ wt}\% \text{Pd}(\text{OAc})_2/\text{C}]$ (100 mg) and NPMoV (15 mg) acidified by $\text{CH}_3\text{SO}_3\text{H}$ (20 mg) in $\text{EtOH} / \text{H}_2\text{O}$ (4.5 / 0.5 mL) at 50°C for 2 h.

In conclusion, Wacker-type oxidation of CP to CPO using O₂ as terminal oxidant was successfully achieved by using a chloride-free reoxidation system under mild conditions. This method provides an alternative useful direct route for the production of CPO from CP easily derived from dicyclopentadiene which is formed in large quantity in the petroleum refining process.

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- Activated carbons available from commercial source: Kurare BP-25 (2420 cm²/g), Kurare coal GLC (1570 cm²/g), Shirasagi (1200 cm²/g) and Darco (650 cm²/g). Molybdovanadophosphate (NPMoV) was prepared according to the literature procedure.^{7a} To a solution of NaVO₃ (7.32 g, 60 mmol) in water (38 mL) was added Na₂MoO₄·2H₂O (18.22 g, 34 mmol) in water (12 mL). To the resulting solution was added 85% H₃PO₄ (7.6 g, 66 mmol) in water (10 mL) and the mixture was heated to 95°C under stirring for 1 h. After cooling to 0°C, a saturated aqueous ammonium chloride (150 mL) was added to the solution to give NPMoV which was purified by the recrystallization from water, and dried in vacuo with heating at about 90°C. The preparation of [Pd(OAc)₂-NPMoV/C] was as follows: Pd(OAc)₂ (333 mg) was dissolved in excess acetone and then activated carbon (3 g) was added. After stirring overnight at room temperature, [Pd(OAc)₂/C] was obtained in quantitative yield. To a suspended water of the [Pd(OAc)₂/C] (3.33 g) was added NPMoV (588 mg), and vigorously stirred for 3 h at room temperature. [Pd(OAc)₂-NPMoV/C] was filtered off, washed with water, and dried in vacuo with heating at about 90°C to give [Pd(OAc)₂-NPMoV/C] in almost quantitative yield.
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