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Molybdovanadophosphate (NPMoV) /hydroquinone/O_2 system as an efficient reoxidation system in palladium-catalyzed oxidation of alkenes

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Abstract

Molybdovanadophosphate (NPMoV)/hydroquinone/O_2 system was found to be an efficient reoxidation system in palladium-catalyzed oxidations of alkenes and related compounds. Thus, acetoxylations of cycloalkenes utilizing molecular oxygen as the final oxidant were cleanly performed using the multicatalytic system consisting of $Pd(OAc)_2$/hydroquinone/NPMoV to form 3-acetoxy-1-cycloalkenes in good yields. For example, cyclopentene and cyclohexene were converted into the corresponding allylic acetates in almost quantitative yields. Omitting hydroquinone from the catalytic system led to low yields of the acetates. Acetoxylation of cyclooctene was satisfactorily achieved by replacing hydroquinone of the multicatalytic system by chlorohydroquinone. Molybdovanadophosphates, which catalyze the smooth dehydrogenation of hydroquinone to benzoquinone with dioxygen, were found to rapidly promote the present Pd(II)-catalyzed acetoxylation of cycloalkenes. By the use of a mixed solvent of ethanol and water under these conditions, Wacker type oxidations of cyclohexene and styrene were accomplished in fair to good yields. Monosubstituted alkenes such as ethyl acrylate and acrylonitrile underwent the acetalization by the present catalytic system to give the corresponding acetals in quantitative yields.

Keywords: Molecular oxygen; Oxidation; Palladium; Molybdovanadophosphate; Quinone; Cycloalkenes

1. Introduction

From synthetic and environmental points of view, the selective oxidation of organic substrates utilizing molecular oxygen as the oxidant is very important and will continue to be an area of great potential in the chemical industry [1]. Cycloalkenes such as cyclohexene undergo palladium(II)-catalyzed allylic acetoxylation in the presence of benzoquinone (BQ) to give 3-acetoxy-1-cycloalkenes [2,3]. In early studies of this oxidation, BQ was used as a stoichiometric reoxidation agent for the Pd(0) reduced in the oxidation cycle to Pd(II) [2]. Thereafter, the acetoxylation of cyclohexene was achieved by the use of a catalytic amount of BQ using MnO_2 as a dehydrogenating agent for the generated hydroquinone (HQ) to BQ [4]. More recently, selective palladium(II)-catalyzed acetoxylations of olefins and dienes used molecular oxygen as the final oxidant have been reported to be accomplished by a combination of BQ and copper(II) acetate [5] or a metal macrocycle [6,7]. It

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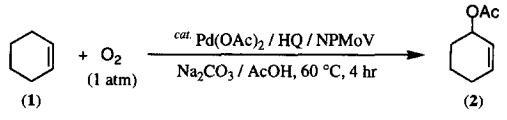
has also been reported that a catalytic system consisting of Pd(II) and iron(III) nitrate promotes the allylic oxidation of cyclohexene with dioxygen [8].

In a previous paper, we have reported that benzylic amines and alcohols can be oxidized with molecular oxygen to Schiff-base imines and carbonyl compounds, respectively, using mixed addenda heteropolyoxometalates (HPM) containing vanadium and molybdenum [9,10]. In the course of the study on the aerobic oxidation using molybdovanadophosphates as catalysts, hydroquinones were smoothly dehydrogenated to quinones with dioxygen by molybdovanadophosphate (NPMoV) partially replaced with ammonium cation [10]. If the NPMoV catalyzes the continuous dehydrogenation of HQ to BQ with molecular oxygen, an alternative chloride-free allylic oxidation system of alkenes by Pd(II) combined with HQ will be developed. Thus, we have examined the Pd(II) catalyzed-oxidation of alkenes using HQ/NPMoV/O_2 as a reoxidizing system for the Pd(0) generated in the oxidation cycle.



(1)

2. Experimental section

2.1. General

All solvents and reagents were purchased from commercial sources and used without further purification unless otherwise noted. Analytical TLC performed on Merck TLC Plastic sheets F_{254} silica gel 60, using UV light and I_2. NMR spectra were recorded on JEOL JNM-EX-270. ^1H and ^{13}C NMR were measured at 270 and 67.5 MHz, respectively, in $CDCl_3$ with Me_4Si as the internal standard. ^{31}P-NMR spectra were obtained in D_2O with H_3PO_4 as an external standard. Infrared spectra (IR) were measured on Perkin Elmer 1600 using a NaCl plate or KBr method. GLC analyses were performed on Shimazu GC-17A equipped with a flame ionization detector using 1 mm × 50 m capillary column (SE-52). All yields were determined by GLC analyses using C_{11} or C_{12} *n*-alkanes as internal standards. Mass spectra were determined on Perkin Elmer Q-Mass 910 at an ionizing voltage of 70 eV. Energy dispersive X-ray analysis was performed with JEOL JEO-2001.

3. Catalysts

Various mixed addenda heteropolyoxometalates, $H_4PMo_{11}VO_{40} \cdot xH_2O$, $H_5PMo_{10}V_2O_{40} \cdot xH_2O$ [11], $(NH_4)_6H_3PV_6W_6O_{40} \cdot 6H_2O$ [12], $H_3PMo_6W_6O_{40} \cdot xH_2O$ [13] were prepared according to literature procedures. Molybdovanadophosphate (NPMoV) partly substituted by ammonium cation was prepared by a modified Pope method [12].

3.1. Molybdovanadophosphate (NPMoV)

To a solution of $NaVO_3$ (7.32 g, 60 mmol) in water (38 mL) was added $Na_2MoO_4 \cdot 2H_2O$ (18.22 g, 34 mmol) in water (12 mL). To the resulting solution was added 85% H_3PO_4 (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 as a brown precipitate. The NPMoV was purified by the recrystallization from water, and dried in vacuo with heating at about 90°C.

From the combustion analysis and ICP measurement, the composition of the NPMoV was found to consist of H 1.76, N 4.76, P 1.91, Mo 23.8, V 24.6%. IR (KBr): 3158, 1621, 1408,

1058, 947, 874, 795 cm^{-1}. The resulting NPMoV was a complex mixture of molybdovanadophosphate partly substituted by ammonium cation having an average atomic ratio of N/P/Mo/V = 5.0/1.0/4.0/4.8.

3.2. NPMoV / C

NPMoV (1 g) was dissolved in excess water (200 mL) and then added 9 g of active charcoal (Wako Pure Chemical Industries, Ltd.; surface area: 1450 m^2/g, pore size (volume): 15–25 Å (0.58 mL/g)). After stirring for 0.5 h at room temperature, NPMoV/C was filtered off, washed with water, and dried in vacuo (20 mmHg) with heating at about 90°C. The NPMoV/C, supporting about 10 wt% of NPMoV on the active charcoal, was obtained in almost quantitative yield (10 g). The surface area and pore volume of NPMoV/C were estimated as 1250 m^2/g and 0.52 mL/g, respectively. IR (KBr): 1059, 943, 854, 777 cm^{-1} (around 1100–700 cm^{-1}). Energy dispersive X-ray spectrum of NPMoV/C showed that NPMoV is homogeneously dispersed with on the active charcoal.

3.3. $Pd(OAc)_2$ / C

$Pd(OAc)_2$ (1 g) was dissolved in excess acetone (300 mL) and then added active charcoal (19 g). After stirring over night at room temperature, $Pd(OAc)_2$/C was filtered off and dried in vacuo with heating at about 60°C. The $Pd(OAc)_2$/C, supporting about 5 wt% of $Pd(OAc)_2$ on the active charcoal, was obtained in almost quantitative yield (20 g).

3.4. [$Pd(OAc)_2$–NPMoV] / C

$Pd(OAc)_2$ (0.44 g) was dissolved in excess acetone (150 mL) and then added active charcoal (10.26 g). After stirring over night at room temperature, $Pd(OAc)_2$/C was filtered off and dried in vacuo with heating at about 60°C. To a suspended water (150 mL) of the $Pd(OAc)_2$/C (10.7 g) was added NPMoV (0.7 g), and vigorously stirred for 0.5 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. The [$Pd(OAc)_2$–NPMoV]/C, supporting 4.1 wt% of $Pd(OAc)_2$ and 6.3 wt% of NPMoV on active charcoal, was obtained in almost quantitative yield (11.4 g).

4. Reactions and products

4.1. Acetoxylation of cycloalkenes

An acetic acid (10 mL) solution of cycloalkene (2 mmol), $Pd(OAc)_2$ (22 mg, 0.1 mmol), hydroquinone (0.4 mmol), NPMoV (35 mg) and Na_2CO_3 (53 mg) was placed in a three-necked flask equipped with a balloon filled with O_2. The mixture was stirred at 60–80°C for 4–15 h. Cooling the reaction mixture to room temperature, water (8 mL) was added and the mixture was extracted with hexane (4 × 15 mL). The combined organic extracts were neutralized with saturated aqueous $NaHCO_3$ (15 mL), then washed with water (2 × 15 mL). The organic layers were dried over anhydrous $MgSO_4$ and carefully concentrated to remain reactants. Acetates were separated by column chromatography over silica gel by hexane-ethyl acetate (gradient up to 10:1), and characterized by IR, ^1H NMR and ^{13}C NMR.

^1H and ^{13}C NMR spectra of acetates, 3-acetoxy-1-cyclohexene (**2**), 3-acetoxy-1-cyclopentene (**4**), 3-acetoxy-1-cycloheptene (**6**), 3-acetoxy-1-cyclooctene (**8**), 3-acetoxy-1-cyclododecene (**10**), 3-acetoxy-5-methyl-1-cyclohexene (**12a**), 3-acetoxy-6-methyl-1-cyclohexene (**12b**) and 3-acetoxy-2-methyl-1-cyclohexene (**14**), were in full accordance with those reported in the literatures [4,14,15].

4.2. Acetoxylation of cis-3a,4,7,7a-tetrahydroindene (15)

15 was oxidized in acetic acid in the presence of $Pd(OAc)_2$ (22 mg, 0.1 mmol), HQ (44 mg,

0.4 mmol), NPMoV (35 mg) and Na_2CO_3 (53 mg) at 60°C for 15 h to form about a 4:1 stereoisomeric mixture of 3-acetoxy-*cis*-3a,4,7,7a-tetrahydroindene (**16**) in 65% yield. **16** (major component): (^{1}H NMR) δ 1.79–1.85 (m, 1H), 2.03 (s, 3H), 2.20–2.35 (m, 4H), 3.07 (m, 1H), 5.35 (dt, 1H), 5.74–5.95 (m, 4H); (^{13}C NMR) δ 21.1, 26.1, 27.0, 42.2, 42.4, 86.3, 127.9, 128.2, 128.7, 142.1, 170.9; IR (NaCl) 3037, 2933, 2841, 1729, 1438, 1362, 1252, 1019, 965, 738, 678 cm^{-1}.

4.3. Oxidation of hydroquinone (HQ) to benzoquinone (BQ)

An acetic acid (10 mL) solution of HQ (220 mg, 2 mmol) and HPM (35–58 mg) or NPMoV/C (350 mg) was placed in a three-necked flask equipped with a balloon filled with O_2. The mixture was stirred at 60°C for 4 h. After cooling the reaction mixture to room temperature, it was neutralized with saturated aqueous $NaHCO_3$ (300 mL) and the mixture was extracted with diisopropyl ether (4 × 30 mL). The combined organic extracts were washed with water (2 × 30 mL). The organic layers were dried over anhydrous $MgSO_4$ and carefully concentrated to remain reactants. BQ was separated by column chromatography over silica gel by hexane-ethyl acetate (gradient up to 10:1), and characterized by IR, ^{1}H NMR and ^{13}C NMR.

4.4. Wacker type oxidation of alkenes

An ethanol/H_2O (19:1) (10 mL) solution of alkene (2 mmol), $Pd(OAc)_2$ (22 mg, 0.1 mmol), HQ (44 mg, 0.4 mmol), NPMoV (35 mg) and CH_3SO_3H (20 mg) was placed in a three-necked flask equipped with a balloon filled with O_2. The mixture was stirred at 50°C for 20 h. Cooling the reaction mixture to room temperature, water (8 mL) was added and the mixture was extracted with hexane (4 × 15 mL). The combined organic extracts were neutralized with saturated aqueous $NaHCO_3$ (15 mL), then washed with water (2 × 15 mL). The organic layers were dried over anhydrous $MgSO_4$ and carefully concentrated to remain reactants. Ketones were separated by column chromatography over silica gel by hexane-ethyl acetate (gradient up to 10:1) to give ketones, which were characterized by IR, ^{1}H NMR and ^{13}C NMR.

4.5. Acetalization of monosubstituted alkenes

An ethanol (10 mL) solution of alkene (2 mmol), $Pd(OAc)_2$ (22 mg, 0.1 mmol), HQ or HQ-Cl (0.4 mmol), NPMoV (35 mg) and CH_3SO_3H (20 mg) was placed in a three-necked flask equipped with a balloon filled with O_2. The mixture was stirred at 60°C for 20 h. Cooling the reaction mixture to room temperature, water (8 mL) was added and the mixture was extracted with diisopropyl ether (4 × 15 mL). The combined organic extracts were neutralized with saturated aqueous $NaHCO_3$, then washed with water (2 × 15 mL). The organic layers were dried over anhydrous Na_2SO_4 and carefully concentrated to remain reactants. Acetals were separated by column chromatography over silica gel by hexane-ethyl acetate (gradient up to 20:1) to give acetals, which were characterized by IR, ^{1}H NMR and ^{13}C NMR.

4.6. Ethyl 3,3-diethoxypropionate (18)

(^{1}H NMR) δ 1.18–1.23 (t, 6H), 1.24–1.29 (t, 3H), 2.65–2.67 (d, 2H), 3.50–3.74 (m, 4H), 4.12–4.20 (q, 2H), 4.94–4.99 (t, 1H); (^{13}C NMR) δ 14.1, 15.1, 39.9, 60.4, 61.8, 99.6, 169.9; IR (NaCl) 2977, 2932, 2901, 1738, 1626, 1446, 1373, 1347, 1311, 1253, 1193, 1062, 937, 843 cm^{-1}.

4.7. Ethyl 2,2-dideuterio-3,3-diethoxypropionate (18-d_2)

(^{1}H NMR) δ 1.18–1.23 (t, 6H), 1.24–1.29 (t, 3H), 3.50–3.74 (m, 4H), 4.12–4.20 (q, 2H), 4.95 (s, 1H); (^{13}C NMR) δ 14.0, 15.1, 39.3,

39.6, 39.8, 60.3, 61.7, 99.5, 169.9; IR (NaCl) 2977, 2931, 2901, 2250, 1733, 1634, 1615, 1446, 1372, 1337, 1267, 1067, 1029, 991, 913, 876 cm^{-1}.

4.8. Cyanoacetaldehyde diethylacetal (20)

(^{1}H NMR) δ 1.21–1.27 (t, 6H), 2.66–2.68 (d, 2H), 3.53–3.77 (m, 4H), 4.77–4.81 (t, 1H); (^{13}C NMR) δ 14.9, 23.9, 62.7, 97.9, 116.3; IR (NaCl) 2980, 2257, 1733, 1374, 1348, 1229, 1121, 1066 cm^{-1}.

4.9. 1,1,3,3-tetraethoxypropane (23)

(^{1}H NMR) δ 1.17–1.23 (t, 12H), 1.93–1.97 (t, 2H), 3.46–3.71 (m, 8H), 4.60–4.64 (t, 2H); (^{13}C NMR) δ 15.2, 38.1, 61.2, 100.2; IR (NaCl) 2976, 2878, 1444, 1377, 1348, 1062, 994, 844 cm^{-1}.

5. Results and discussion

In the present work, molybdovanadophosphate (NPMoV) partly substituted by ammonium cation, which was prepared according to the Pope method [12], was employed as catalyst. From the combustion analysis and ICP measurement, it was found that NPMoV consists of an average atomic ratio of N/P/Mo/V = 5.0/1.0/4.0/7.8.

The ^{31}P NMR of the resulting NPMoV gave a number of signals which show that the NPMoV is a complex mixture of molybdovanadophosphate (Fig. 1). In order to obtain a molybdovanadophosphate consisting of a single composition, purification of the resulting NPMoV was examined by carrying out repeated recrystallization from water and sulfuric acid differing pH (pH 1–3), but we were not able to obtain a molybdovanadophosphate having a single composition. Thus, NPMoV obtained by recrystallization twice from water was used as catalyst in the present oxidation.

The acetoxylation of cyclohexene (**1**) was chosen as a model reaction and carried out under various reaction conditions. When **1** was allowed to react in the presence of $Pd(OAc)_2$, HQ and NPMoV in acetic acid under oxygen atmosphere (1 atm) at 60°C for 4 h (standard conditions), it was found that 3-acetoxy-1-cyclohexene (**2**) was obtained in quantitative yield (> 99%) (Eq. (1)) (Table 1). This finding suggests that various heteropolyoxometalates (HPM) can probably also be used as reoxidation catalysts in this oxidation. From the inspection of various HPM, $H_5PMo_{10}V_2O_{40}$ was found to promote the rapid acetoxylation of **1** to **2** in high yield (run 7). $H_4PMo_{11}VO_{40}$ was also effi-

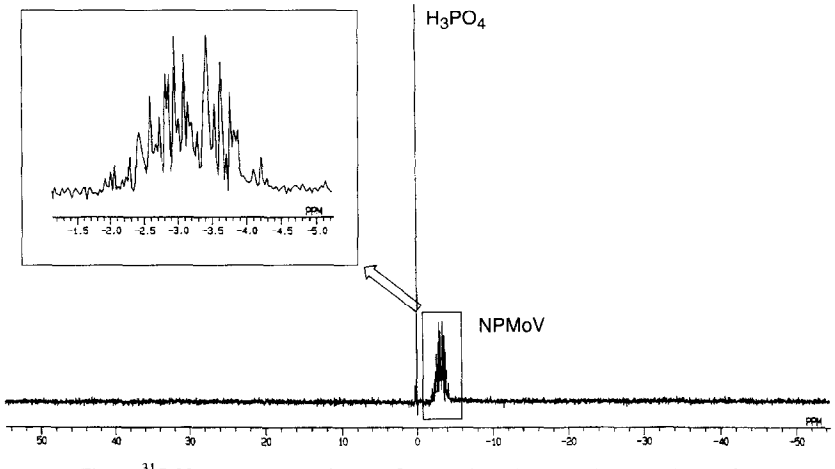


Fig. 1. ^{31}P NMR spectrum of NPMoV in D_2O with external standard, H_3PO_4.

Table 1
Acetoxylation of cyclohexene (**1**) to 3-acetoxy-1-cyclohexene (**2**) by Pd(II)/HQ/HPM/O_2 system [a]

Run	HPM (mg)	Pd(II)	Yield (%)
1	NPMoV (35)	$Pd(OAc)_2$	> 99
2 [b]	NPMoV (35)	$Pd(OAc)_2$	27
3	NPMoV (35)	$PdCl_2$	25
4	NPMoV (35)	$PdSO_4$	83
5	NPMoV/C (350)	$Pd(OAc)_2$	81
6 [c]	$H_4PMo_{11}VO_{40}$ (36)	$Pd(OAc)_2$	96
7 [d]	$H_5PMo_{10}V_2O_{40}$ (35)	$Pd(OAc)_2$	93
8	$(NH_4)_6H_3PV_6W_6O_{40}$ (46)	$Pd(OAc)_2$	19
9	$H_3PMo_6W_6O_{40}$ (47)	$Pd(OAc)_2$	8
10	$H_3PMo_{12}O_{40}$ (37)	$Pd(OAc)_2$	7
11	$H_3PW_{12}O_{40}$ (58)	$Pd(OAc)_2$	5

[a] **1** (2 mmol) was allowed to react in the presence of Pd(II) (0.1 mmol), HQ (0.4 mmol), HPM and Na_2CO_3 (53 mg) in acetic acid (10 mL) under oxygen atmosphere (1 atm) at 60°C for 4 h.
[b] In the absence of HQ.
[c] Reaction time was 2 h.
[d] Reaction time was 1 h.

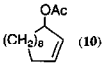
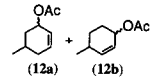
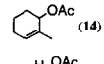
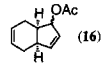
cient in the acetoxylation of **1** to **2** (run 6), but $(NH_4)_6H_3PV_6W_6O_{40}$ and $H_3PMo_6W_6O_{40}$ were less efficient than NPMoV (runs 8 and 9). Typical heteropolyacids such as $H_3PM_{12}O_{40}$ (M = Mo or W) were inactive in this oxidation to give poor yields of **2**. Based on the examination of Pd(II) salts in the present transformation, $Pd(OAc)_2$ could be replaced by $PdSO_4$ but not $PdCl_2$ under these reaction conditions. The combination of $PdCl_2$ and NPMoV resulted in a significant decrease in **2** (25%) (run 3), but replacing the former with $PdSO_4$ restored the formation of **2** (83%) (run 4). The acetoxylation by the supported catalyst, NPMoV/C, afforded **2** in satisfactory yield (81%) (run 5).

It has been reported that aerobic oxidations of ethylene to acetaldehyde and cyclohexene to cyclohexanone are promoted by $Pd(II)/H_{3+n}PMo_{12-n}V_nO_{40}$ [16] and $Pd(II)/H_3PMo_6W_6O_{40}$ [17] systems, respectively, in the absence of HQ, but the present oxidation gave **2** in low yield (27%) when HQ was omitted (run 2). This fact indicates that the Pd(0) reduced in the oxidation cycle is hardly reoxidized to Pd(II) with molecular oxygen by NPMoV alone under these reaction conditions.

On the basis of these results, a variety of cycloalkenes were acetoxylated by the use of $Pd(OAc)_2/HQ/NPMoV/O_2$ system in acetic acid under selected reaction conditions (Table 2).

The reactivity of cycloalkenes was found to depend markedly on their ring sizes. This is best illustrated by comparing the reactivity between **1** and cyclooctene (**7**) as shown later. In a manner similar to that for **1**, cyclopentene (**3**) was cleanly converted into 3-acetoxy-1-cyclopentene (**4**) in excellent yield (98%). Unlike **1** and **3**, the acetoxylation of cycloheptene (**5**) proceeded somewhat slowly under the standard conditions to form 3-acetoxy-1-cycloheptene (**6**) in 62%, but **6** was obtained in satisfactory yield when the reaction was prolonged to 12 h (86%) or carried out at 70°C for 6 h (93%) (runs 3 and 4). Cyclooctene **7** was rather unreactive under

Table 2
Acetoxylation of various cycloalkenes by $Pd(OAc)_2$/HQ/NPMoV/O_2 system [a]

Run	Cycloalkene	Time / hr	Temp / °C	Product	Yield / %
1	Cyclopentene (**3**)	4	60	 (**4**)	98
2	Cycloheptene (**5**)	4	60	 (**6**)	62 (92)[b]
3	**5**	12	60	**6**	86
4	**5**	6	70	**6**	93
5	Cyclooctene (**7**)	4	60	 (**8**)	9 (24)[b]
6	**7**	15	80	**8**	55 (78)[b]
7	Cyclododecene (**9**)	15	80	 (**10**)	77 (86)[b]
8	 (**11**)	4	60	 (**12a**) + (**12b**)	80 + 10
9	 (**13**)	6	70	 (**14**)	43 (84)[b]
10	 (**15**)	15	60	 (**16**)	65 (88)[b]

[a] Cycloalkene (2 mmol) was allowed to react in the presence of $Pd(OAc)_2$ (0.1 mmol), HQ (0.4 mmol), NPMoV (35 mg) and Na_2CO_3 (53 mg) in acetic acid (10 mL) under oxygen atmosphere (1 atm).
[b] Number of parentheses shows the selectivity of products.

the standard conditions. Thus, **7** was allowed to react under somewhat severe reaction conditions (at 80°C for 15 h) to form 3-acetoxy-1-cyclooctene (**8**) in 55%. It has also been mentioned that **7** was difficult to oxidize by the Pd(II)/BQ/MnO_2 system to form **8** in low yield [4]. In order to reveal the influence of the methyl substituent on the cyclohexene ring, the acetoxylation of 4-methylcyclohexene (**11**) and 1-methylcyclohexene (**13**) was examined. **11** was more reactive than **13**, and was smoothly oxidized under standard conditions to form about an 8:1 regioisomeric mixture of 3-acetoxy-5-methyl-1-cyclohexene (**12a**) and 3-acetoxy-6-methyl-1-cyclohexene (**12b**) in 90% yield. In addition, **13** was oxidized with complete regioselectivity to give 2-methyl-3-acetoxycyclohexene (**14**), although the yield was low (43%). In the case of *cis*-3a,4,7,7a-tetrahydroindene (**15**) having cyclohexene and cyclopentene rings, the acetoxylation occurred exclusively at the cyclopentene double bond to form the corresponding 3-acetoxy derivative **16** consisting of about a 4:1 stereoisomeric mixture. The orientation of the acetoxy group of the major component in **16** may be directed to sterically favorable anti-configuration.

To improve the yield of **8** using the present oxidation system, several different hydroquinones were examined (Table 3). As a result of the inspection of several hydroquinones, we found that chlorohydroquinone (HQ-Cl) serves as a good mediator of the acetoxylation of **7**. The yield of **8** was improved to 83% when HQ-Cl was used in place of HQ (run 2). On the other hand, when methyl- and trimethylhydroquinones (HQ-Me and HQ-Me_3) were used as hydroquinones, the results sharply contrasted with the behavior of the HQ-Cl. Acetoxylations of **7** by the use of HQ-Me and HQ-Me_3 were considerably retarded to form **8** in 42% and 13%, respectively (runs 3 and 4). The combination of $PdCl_2$ and HQ-Cl was also unfavorable for the acetoxylation of **7**, but the use of $PdSO_4$ and HQ-Cl resulted in almost the same results as $Pd(OAc)_2$ (runs 5 and 6). In a manner similar to that for the acetoxylation of **1** using $H_5PMo_{10}V_2O_{40}$, **8** was rapidly acetoxylated by $H_5PMo_{10}V_2O_{40}$ under these conditions to form **11** in 85% yield (run 7).

In a previous paper, we showed that the catalytic activities of molybdovanadophosphates in the oxidation of hydroquinones and phenols with dioxygen were markedly enhanced by supporting the catalyst on active charcoal [18] (Table 4). Thus, the acetoxylation of **1** was carried out using NPMoV/C in place of NPMoV under the standard conditions, but the yield of **2** was slightly decreased compared to that by NPMoV

Table 3
Acetoxylation of cyclooctene (**7**) to 3-acetoxy-1-cyclooctene (**8**) using several kinds of hydroquinones by $Pd(OAc)_2$/hydroquinone/NPMoV/O_2 system [a]

Run	Pd(II)	Hydroquinone	Conv. (%)	Yield (%)
1	$Pd(OAc)_2$	HQ	70	55
2	$Pd(OAc)_2$	HQ-Cl	96	83
3	$Pd(OAc)_2$	HQ-Me	62	42
4	$Pd(OAc)_2$	HQ-Me_3	52	13
5	$PdCl_2$	HQ-Cl	71	19
6	$PdSO_4$	HQ-Cl	96	82
7 [b,c]	$Pd(OAc)_2$	HQ-Cl	98	85
8 [b,c]	$PdSO_4$	HQ-Cl	> 99	71

[a] **7** (2 mmol) was allowed to react in the presence of Pd(II) (0.1 mmol), hydroquinone (0.4 mmol), NPMoV (35 mg) and Na_2CO_3 (53 mg) in acetic acid (10 mL) under oxygen atmosphere (1 atm) at 80°C for 15 h.
[b] $H_5PMo_{10}V_2O_{40}$ (35 mg) was used instead of NPMoV.
[c] Reaction time was 4 h.

Table 4
Acetoxylation of cyclohexene (**1**) to 3-acetoxy-1-cyclohexene (**2**) by supported catalysts [a]

Run	Pd(II)	HPM	Yield (%) [b]
1	$Pd(OAc)_2$	NPMoV	> 99
2	$Pd(OAc)_2$	NPMoV/C	81
3	$Pd(OAc)_2$/C	NPMoV	45 (76)
4	$Pd(OAc)_2$/C	NPMoV/C	45 (73)
5	[$Pd(OAc)_2$–NPMoV]/C		76 (98)
6	recovered [$Pd(OAc)_2$–NPMoV]/C		(88)

[a] **1** (2 mmol) was allowed to react in the presence of HQ (0.4 mmol), $Pd(OAc)_2$ (0.1 mmol) (or $Pd(OAc)_2$/C (440 mg)) and NPMoV (35 mg) (or NPMoV/C (350 mg)), or in the presence of HQ (0.4 mmol) and [$Pd(OAc)_2$–NPMoV]/C (570 mg) in acetic acid (10 mL) under oxygen atmosphere (1 atm) at 60°C for 4 h.
[b] Number of parentheses shows the yield of **2** after 20 h.

Table 5
Aerobic oxidation of hydroquinone (HQ) to benzoquinone (BQ) by various HPM catalysts [a]

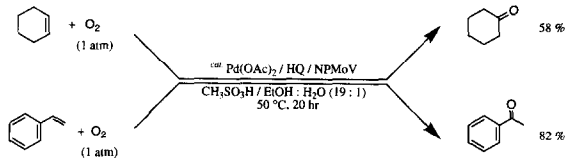
Run	HPM (mg)	Yield (%)
1	NPMoV (35)	45
2	NPMoV/C (350)	82
3	$H_4PMo_{11}VO_{40}$ (36)	62
4	$H_5PMo_{10}V_2O_{40}$ (35)	65
5	$(NH_4)_6H_3PV_6W_6O_{40}$ (46)	9
6	$H_3PMo_6V_6O_{40}$ (47)	6
7	$H_3PMo_{12}O_{40}$ (37)	23
8	$H_3PW_{12}O_{40}$ (58)	2

[a] HQ (2 mmol) was allowed to react in the presence of HPM in acetic acid (10 mL) under oxygen atmosphere (1 atm) at 60°C for 4 h.

(run 2). However, when $Pd(OAc)_2$/C was employed instead of $Pd(OAc)_2$, the yield of **2** became 76%. By supporting both $Pd(OAc)_2$ and NPMoV on the active charcoal, **1** was converted into **2** in 98% yield, although a somewhat longer reaction time (20 h) was needed. The oxidation of **1** by the recovered [$Pd(OAc)_2$–NPMoV]/C catalyst gave **2** in 88% yield.

In the acetoxylation of cycloalkenes by the present multicatalytic system, it is considered that the smooth dehydrogenation of hydroquinones to benzoquinones with molecular oxygen by molybdovanadophosphate catalysts is an essential step in this transformation. Thus, the catalytic potential of HPM for the dehydrogenation of HQ to BQ with molecular oxygen was evaluated (Table 5). Among the catalysts examined, $H_5PMo_{10}V_2O_{40}$ was the most efficient catalyst followed by $H_4PMo_{11}VO_{40}$ > NPMoV > $(NH_4)_6H_3PV_6W_6O_{40}$. The order of the catalytic activity of HPM for the dehydrogenation of HQ to BQ was essentially the same as obtained for the acetoxylation of **1** to **2**. This observation strongly suggests that the rate controlling step in the acetoxylation by the present catalytic system is the dehydrogenation of HQ to BQ with dioxygen by HPM.

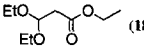
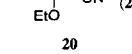
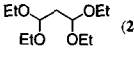
The present catalytic system could be extended to the Wacker type oxidation. For example, **1** and styrene were oxidized in ethanol/H_2O (19:1) acidified with CH_3SO_3H under otherwise identical conditions to those of the acetoxylation of **1**, giving cyclohexanone and acetophenone in 58% and 82% yields, respectively (Eq. (2)).



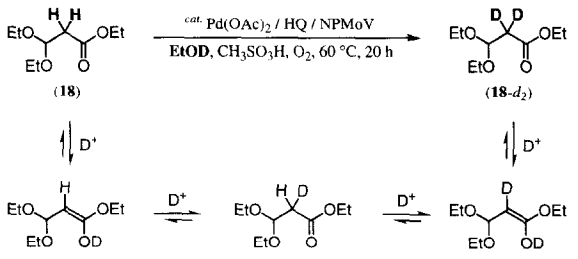
(2)

On the other hand, the acetalization of acrylonitrile and acrylate under the influence of Pd(II) has been carried out in an industrial process [19], because acetals derived from these substrates have become important intermediates in synthetic organic chemistry, in particular the pharmaceutical chemistry. In the course of the palladium-catalyzed allylic acetoxylation of olefins, the present Pd(II)/HQ/NPMoV/O_2 system was found to apply to acetalization of monosubstituted alkenes such as ethyl acrylate

Table 6
Acetalization of various monosubstituted alkenes by $Pd(OAc)_2$ /hydroquinone/NPMoV/O_2 system [a]

Run	Substrate	Hydroquinone	Product	Yield / %
1	 (17)	HQ	 (18)	> 99
2[b]	17	HQ	18	2
3	 (19)	HQ	 (20)	20
4	19	HQ-Cl	20	> 99
5[b]	19	HQ-Cl	20	15
6	 (21)	HQ	 (23)	38
7	 (22)	HQ-Cl	23	58
8[b]	22	HQ-Cl	23	5

[a] Substrate (2 mmol) was allowed to react in the presence of $Pd(OAc)_2$ (0.1 mmol), HQ or HQ-Cl (0.4 mmol), NPMoV (35 mg) and CH_3SO_3H (20 mg) in ethanol (10 mL) under oxygen atmosphere (1 atm) at 60°C for 20 h.
[b] $H_5PMo_{10}V_2O_{40}$ was used instead of NPMoV.

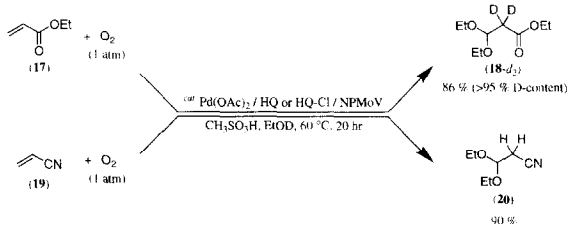


Scheme 1. Exchange of proton in acetal (**18**) with EtOD.

(**17**) and acrylonitrile (**19**). Table 6 shows the representative results for the acetalization of several different types of substituted olefins by the $Pd(OAc)_2/HQ/NPMoV/O_2$ system.

The reaction of **17** in ethanol acidified with CH_3SO_3H under the influence of $Pd(OAc)_2$ using $HQ/NPMoV/O_2$ as the reoxidation catalyst afforded ethyl 3,3-diethoxypropionate (**18**) in quantitative yield. In the case of **19**, cyanoacetaldehyde diethylacetal (**20**) was obtained in quantitative yield using HQ-Cl in place of HQ. Acrolein (**21**) and acrolein diethylacetal (**22**) in ethanol afforded the same product, 1,1,3,3-tetraethoxypropane (**22**), corresponding to the diacetal of malonaldehyde in moderate yields. In contrast to the acetoxylation of **1** and **7** where $H_5PMo_{10}V_2O_{40}$ showed higher catalytic activity, in the acetalization of **17**, **19** and **22** this catalyst led to the production of acetals in 2–15% yields. Unfortunately, the question of its ineffectiveness remains open.

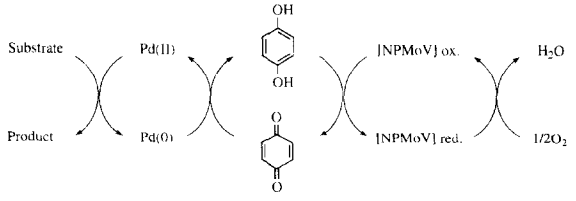
The reaction mechanism of the Pd(II)-catalyzed acetalization has been reported in detail by Hosokawa et al. [20]. Based on consideration of the acetalization of **17** and **19** in ethyl alcohol-d_1 (EtOD) by the present catalytic system, the reaction is also explained by a similar reaction path proposed by the above author. It is interesting to note that the acetalization of **17** in EtOD gave ethyl 2,2-dideuterio-3,3-diethoxypropionate (**18**-d_2) in which two deuterium atoms are incorporated at more than 95% on the C-2 position (Eq 3). In contrast, no deuterium incorporation was observed in the acetalization of acrylonitrile **19**. To obtain more information on the formation of acetal **18**-d_2 in the acetalization of **17** in EtOD, acetal **18** was treated in EtOD under the same conditions as the acetalization. The ^{1}H-NMR spectrum of the recovered acetal **18** shows that a large part of **18** was deuterated to **18**-d_2. This finding indicates that the proton on the C-2 position of **18** is easily exchanged with deuterium in EtOD under these reaction conditions, probably through enol-keto tautomerism (Scheme 1). In fact the same treatment of **18** even in the absence of $Pd(OAc)_2$ and NPMoV afforded 25% of **18**-d_2. In the case of acrylonitrile **19**, no deuterium was incorporated in acetal **20**, since the **20** is not enolizable as is **18**.



(3)

The outline of the oxidation of alkenes by the present multicatalytic system is shown as Scheme 2. BQ serves as a good oxidizing agent of the reduced palladium(0) in the reaction cycle to disproportionate to palladium(II) and HQ which then is dehydrogenated to BQ with dioxygen by NPMoV.

In conclusion, a selective process for aerobic oxidation of several different types of alkenes by a multicatalytic system consisting of Pd(II)/HQ/NPMoV has been developed. This process is based on the principle of electron



Scheme 2. Aerobic oxidation of olefinic compound by multicatalytic system using Pd(II)/HQ/NPMoV.

transfer via a coupled redox system similar to that occurring in biological systems and provides an alternative method for acetoxylation of various cycloalkenes and for acetalization of monosubstituted alkenes.

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References

[1] R.A. Sheldon and J.K. Kochi, Metal-Catalyzed Oxidations of Organic Compounds (Academic Press, New York, 1981); C.L. Hill, Activation and Functionalization of Alkanes (Wiley Interscience, New York, 1989); L. Simandi, catalytic Activation of Dioxygen by Metal Complexes (Kluwer Academic Publisher, 1992); P.H.R. Barton, A.E. Martell and D.T. Sawyar (Eds.), The Activation of Dioxygen and Homogeneous Catalytic Oxidation (Plenum Press, New York, 1993).

[2] A. Hewmann and B. Åkermark, Angew. Chem. Int. Ed. Engl. 23 (1984) 453.

[3] R.G. Broun and J.M. Davidson, J. Chem. Soc. A (1971) 1321.

[4] S. Hansson, A. Heumann, T. Rein and B. Åkermark, J. Org. Chem. 55 (1990) 975.

[5] S.E. Byström, E.M. Larsson and B. Åkermark, J. Org. Chem. 55 (1990) 5674.

[6] J.-E. Bäckvall, R.B. Hopkins, H. Grennberg, M.M. Mader and A.K. Awasthi, J. Am. Chem. Soc. 112 (1990) 5160.

[7] H. Grennberg, V. Simon and J.-E. Bäckvall, J. Chem. Soc. Chem. Commun. (1994) 265.

[8] E.M. Larsson and B. Åkermerk, Tetrahedron Lett. 34 (1993) 2523.

[9] K. Nakayama, M. Hamamoto, Y. Nishiyama and Y. Ishii, Chem. Lett. (1993) 1699.

[10] M. Hamamoto, K. Nakayama, Y. Nishiyama and Y. Ishii, J. Org. Chem. 58 (1993) 6421.

[11] G.E. Tsigdinos and C.J. Hallada, Inorg. Chem. 7 (1968) 437.

[12] D.P. Smith and M.T. Pope, Inorg. Chem. 12 (1973) 331.

[13] J.C. Bailar, Jr., Inorg. Chem. 1 (1939) 132.

[14] A.J. Person and S.Y. Hsu, J. Org. Chem. 51 (1986) 2505.

[15] Y.L. Chow and G.E. Buono-Core, J. Am. Chem. Soc. 108 (1986) 1234.

[16] K.I. Matveev, Kinet. Catal. 18 (1977) 862.

[17] H. Ogawa, H. Fujinami, K. Taya and S. Teratani, Bull. Chem. Soc. Jpn. 57 (1984) 1908.

[18] S. Fujibayashi, K. Nakayama, Y. Nishiyama and Y. Ishii, Chem. Lett. (1994) 1345.

[19] M. Yamashita and H. Asada, A New Route to Acetal Compounds, in: B. Pearson (Eds.), Speciality Chemicals (Elsevier, 1991) p. 423.

[20] T. Hosokawa, T. Yamanaka, M. Itotani and S.-I. Murahashi, J. Org. Chem. 60 (1995) 6159 and references cited therein.