

# Palladium(II)-catalyzed oxidation of terminal alkenes to methyl ketones using molecular oxygen

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Received (in Cambridge, UK) 7th March 2000, Accepted 18th April 2000

Published on the Web 31st May 2000

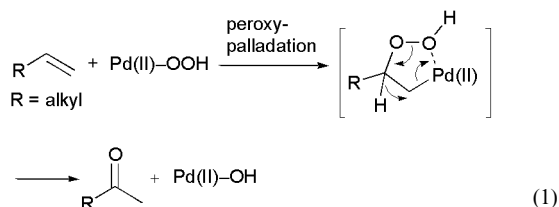
Palladium(II) acetate catalyzes the aerobic oxidation of terminal alkenes in toluene into the corresponding methyl ketones in the presence of a catalytic amount of pyridine using propan-2-ol as a reductant and molecular oxygen as an oxidant. Two catalytic cycles sharing a Pd(II)-OOH species are proposed. One is the formation of a Pd(II)-H species in the oxidation of propan-2-ol to acetone, followed by reaction with molecular oxygen to give a Pd(II)-OOH species, and the other is peroxy-palladation of an alkene with the Pd(II)-OOH species produced to afford a methyl ketone in the presence of H<sub>2</sub>O<sub>2</sub> produced by the former catalytic cycle.

## Introduction

Palladium-catalyzed oxidation of alkenes to methyl ketones has been developed in synthetic organic chemistry as well as in industrial processes, and is well-known in the Wacker process using PdCl<sub>2</sub> and CuCl<sub>2</sub> or Cu<sub>2</sub>Cl<sub>2</sub> as catalysts in acidic water under an oxygen atmosphere.<sup>1</sup> However, this catalytic system is highly corrosive because of its acidic conditions and may cause the formation of chlorinated by-products. To overcome such drawbacks, halide-free catalytic systems have also been widely investigated;<sup>2-5</sup> e.g. the combination of benzoquinone and iron(II) phthalocyanine<sup>2</sup> or molybdovanadophosphate,<sup>3</sup> the Pd(II)salt-heteropolyacid system,<sup>4</sup> and the Pd(II) salt-polyanilines or polypyrrole system.<sup>5</sup> Furthermore, a recent report of aerobic oxidation in water using a water soluble palladium complex and a base showed very high selectivity of the product as well as effective catalyst recycling.<sup>6</sup>

Typical Wacker-type catalysis has been extensively studied and it is believed that Pd(II) is reduced to Pd(0) and the use of a reoxidant such as the combination of a copper salt and O<sub>2</sub> is indispensable for the catalysis by palladium.<sup>1</sup> On the other hand, an alternative mechanism has also been proposed, in which a formal oxidation state of Pd(II) remains throughout the reaction *via* the formation of a Pd(II)-OOH species by O<sub>2</sub> insertion to an initially produced Pd(II)-H species.<sup>7</sup>

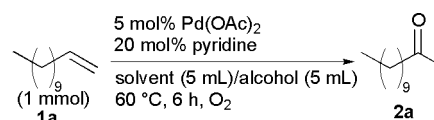
Mimoun and co-workers have reported that the Pd(II)-OOH species undergoes an oxygen transfer to terminal alkenes through a five-membered pseudocyclic peroxy-palladation mechanism [eqn. (1)].<sup>8</sup> They also investigated this reaction



systematically to develop an efficient catalytic procedure for the oxidation of terminal alkenes to methyl ketones using a palladium catalyst and 30% aqueous H<sub>2</sub>O<sub>2</sub> as a stoichiometric oxidant.<sup>8b</sup>

An example of the palladium-catalyzed oxidation of cyclopentene to cyclopentanone in ethanol using molecular oxygen as the sole reoxidant was reported by Takehira and

**Table 1** Pd(II)-catalyzed oxidation of dodec-1-ene to dodecan-2-one by molecular oxygen



Entry	Solvent	Alcohol	Conversion (%)	GLC yield (%) <sup>a</sup>
1	Toluene	Methanol	6	2
2	Toluene	Ethanol	26	14
3	Toluene	Propan-2-ol	84	70
4	THF	Propan-2-ol	18	11
5	1,4-Dioxane	Propan-2-ol	22	14

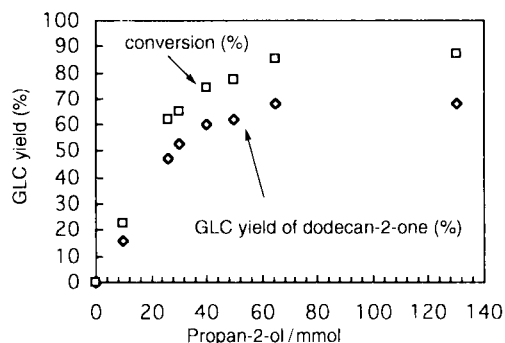
<sup>a</sup> Based on the amount of dodec-1-ene employed.

co-workers in 1985. They also proposed the formation of a Pd(II)-OOH species from palladium, ethanol and oxygen.<sup>9</sup>

Recently, we reported the aerobic oxidation of alcohols in toluene to the corresponding aldehydes and ketones using a catalytic amount of Pd(OAc)<sub>2</sub> and pyridine under an oxygen atmosphere, in which we proposed that a Pd(II)-OOH species was produced *in situ* by the reaction of a Pd(II)-H species with O<sub>2</sub>.<sup>10</sup> We have now applied our Pd(OAc)<sub>2</sub>-pyridine-O<sub>2</sub> catalytic system to the oxidation of alkenes. We report herein the palladium-catalyzed aerobic oxidation of alkenes to the corresponding methyl ketones using a suitable alcohol as a reductant for the formation of a Pd(II)-H species.<sup>11</sup>

## Results and discussion

Dodec-1-ene (**1a**) was chosen first as a substrate to determine the optimum conditions. At first, the reaction was attempted in different solvents using three alcohols as reductants. The reaction procedure was as follows: to a mixture of 5 mol% Pd(OAc)<sub>2</sub>, 20 mol% pyridine, solvent (5 mL) and alcohol (1 mL) was added **1a** (1 mmol) in alcohol (4 mL) at 60 °C and the mixture was stirred for 6 h under an oxygen atmosphere. The results are summarized in Table 1. Among the three alcohols examined in toluene as solvent, propan-2-ol was found to be most effective for the formation of the expected dodecan-2-one (**2a**) (70% GLC yield; Table 1, entry 3), and solvents other than toluene, such as tetrahydrofuran (THF) and 1,4-dioxane,



**Fig. 1** The effect of the amount of propan-2-ol. *Reagents and conditions:* Pd(OAc)<sub>2</sub> (0.05 mmol), dodec-1-ene (1.0 mmol), pyridine (0.2 mmol), toluene (5 mL), propan-2-ol, O<sub>2</sub>, 60 °C, 6 h.

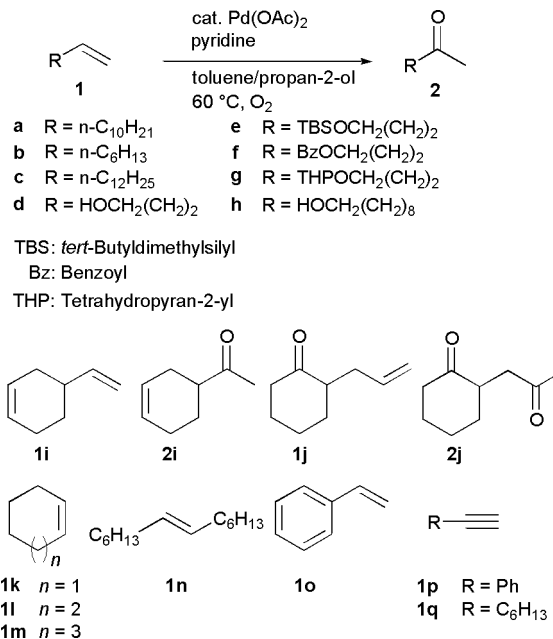
**Table 2** The effect of the amount of pyridine on the oxidation of dodec-1-ene<sup>a</sup>

Entry	Pyridine/mmol	Conversion (%)	GLC yield (%) <sup>b</sup>
1	0.1	85	58
2	0.2	84	70
3	0.3	53	43
4	0.4	51	40

<sup>a</sup> *Reagents and conditions:* Pd(OAc)<sub>2</sub> (0.05 mmol), dodec-1-ene (1.0 mmol), pyridine, toluene (5 mL), propan-2-ol (5 mL), O<sub>2</sub>, 60 °C, 6 h.  
<sup>b</sup> Based on the amount of dodec-1-ene employed.

were revealed to be ineffective even when using propan-2-ol (entries 4 and 5). Next, we examined the effect of the amount of pyridine, because its presence was revealed to be an essential factor for the oxidation of alcohols in our previous studies.<sup>10b</sup> When 0.1 mmol of pyridine (2 equiv. to Pd(OAc)<sub>2</sub>) were used, the conversion of **1a** was fast, but in this case the precipitation of metallic palladium was observed, resulting in a reduction in product selectivity, probably due to the isomerization of **1a** to internal alkenes<sup>12</sup> (Table 2, entry 1). The use of 4 equiv. of pyridine gave **2b** in good yield (70%) and selectivity (83%) (entry 2). On the other hand, the presence of a greater excess of pyridine decreased the reaction rate (entries 3 and 4). The amount of propan-2-ol is another crucial factor for this reaction. When the reaction was performed with less than 65 mmol (5 mL) of propan-2-ol, the reaction rate decreased, while a large excess of propan-2-ol did not affect the product yield or its selectivity (Fig. 1). Although various kinds of dehydrating reagents, such as Na<sub>2</sub>SO<sub>4</sub>, CaSO<sub>4</sub>, CaO, MgSO<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub>, NaOAc, Na<sub>2</sub>CO<sub>3</sub>, SiO<sub>2</sub>, and K<sub>2</sub>CO<sub>3</sub>, were added to the reaction mixture in the hope of increasing the yield and selectivity, all of them were revealed to be ineffective.

The results of the application of this optimized procedure to a variety of terminal alkenes (**1a–1j**; Scheme 1) are shown in Table 3. At higher temperatures such as at 80 °C using propan-2-ol as a reductant, the reaction became sluggish and the product yield decreased.<sup>13</sup> However, butan-2-ol could be used for this oxidation at 75 or 80 °C and slightly better yields were obtained in a shorter reaction time (Table 3, entries 2, 10, 15 and 17). The amount of Pd(OAc)<sub>2</sub> could also be reduced to 2.5 mol%, but a longer reaction time was required (entry 3). Other simple terminal alkenes, such as oct-1-ene (**1b**) and tetradec-1-ene (**1c**), were oxidized to octan-2-one (**2b**) and tetradecan-2-one (**2c**) in good yields, respectively (entries 5 and 6). Pent-4-en-1-ol (**1d**) yielded 5-hydroxypentan-2-one (**2d**) in 21% isolated yield in spite of the high conversion of **1d**, probably due to the formation of the product by an intramolecular Wacker-type reaction (entry 7).<sup>14</sup> However, this catalyst system showed compatibility with a hydroxy protecting group, such as *tert*-butyldimethylsilyl (**1e**), benzoyl (**1f**), and tetrahydropyranyl (**1g**) (entries 8–11). Interestingly, undec-10-en-1-ol (**1h**) was mainly transformed into 11-hydroxyundecan-2-one (**2h**) in 71%



**Scheme 1**

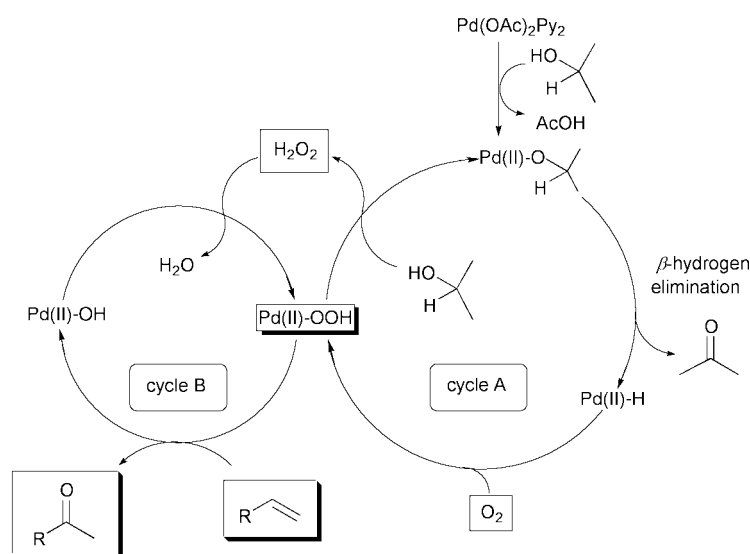
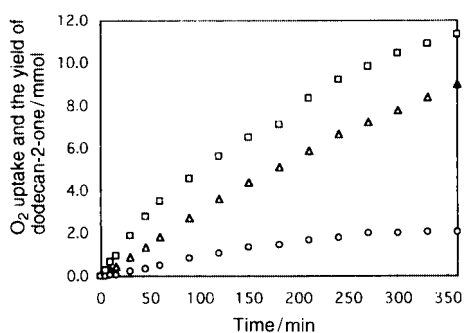
yield showing that terminal alkenes are oxidized much faster than hydroxy groups.<sup>15</sup> It is noteworthy that this oxidation system was applicable to terminal alkenes, but not to internal ones (entries 13–15, Table 3): *i.e.*, the terminal alkene group of **1i** was selectively oxidized to give cyclohex-3-en-1-yl methyl ketone (**2i**) in 75% yield.<sup>16</sup> Unfortunately, in the oxidation of 2-allylcyclohexan-1-one (**1j**), the corresponding 1,4-diketone **2j** (which is a useful precursor for the synthesis of cyclopentanones<sup>17</sup>) was obtained only in low yield with other unidentified by-products (entries 16 and 17). Cyclic internal alkenes such as cyclohexene (**1k**), cycloheptene (**1l**), and cyclooctene (**1m**) were not oxidized and neither was (*E*)-tetradec-7-ene (**1n**). When the oxidation of styrene (**1o**) or terminal alkynes (**1p** and **1q**) was attempted, the reaction mixture turned black and afforded many unidentified products.

A plausible pathway for this oxidation using a Pd(OAc)<sub>2</sub>–pyridine–propan-2-ol–O<sub>2</sub> catalytic system is shown in Scheme 2. In this mechanism, two catalytic cycles operate. One cycle is the oxidation of propan-2-ol (cycle A) to give acetone and a Pd(II)–H species, the latter of which is transformed to a Pd(II)–OOH species by the reaction with oxygen. The Pd(II)–OOH species reacts with an alcohol to give the alkoypalladium(II) species as well as H<sub>2</sub>O<sub>2</sub>.<sup>10b</sup> This Pd(II)–OOH species also reacts with alkenes *via* a pseudocyclic intermediate [eqn. (1), peroxy-palladation] in another catalytic cycle (cycle B) to produce methyl ketones and a Pd(II)–OH species which reacts with H<sub>2</sub>O<sub>2</sub> to give again the Pd(II)–OOH species.<sup>8b</sup> In order to obtain the best result, it was important to add the alkene *ca.* 5 min after the addition of propan-2-ol (see Experimental section). This is because the low concentration of H<sub>2</sub>O<sub>2</sub> may retard the reproduction of the Pd(II)–OOH species from the Pd(II)–OH species, which could react with an alkene to give a stable  $\pi$ -allylpalladium complex and thus reduce the ketone yield. The production of H<sub>2</sub>O<sub>2</sub> was detected by a KI/starch test of the reaction mixture after oxidation of dodec-1-ene for 6 h, and therefore supports our plausible pathway. Fig. 2 shows the relationship between O<sub>2</sub> uptake and dodecan-2-one produced in the oxidation of dodec-1-ene. O<sub>2</sub> uptake in the oxidation of propan-2-ol (15 mL, 196 mmol) to acetone in toluene (15 mL) without dodec-1-ene using 5 mol% Pd(OAc)<sub>2</sub> and 20 mol% pyridine under oxygen was revealed to be *ca.* 9 mmol after 6 h, while an O<sub>2</sub> uptake of *ca.* 11 mmol was observed in the presence of dodec-1-ene (3 mmol). This result shows that the oxidation of propan-2-ol is accelerated by the presence of dodec-1-ene because of the increase in consumption of the Pd(II)–OOH

**Table 3** Pd(II)-catalyzed oxidation of terminal alkenes to methyl ketones by molecular oxygen<sup>a</sup>

Entry	Substrate	Alcohol	Reaction temp/°C	Reaction time/h	Product	Conversion (%)	Isolated yield (%) <sup>b</sup>
1	<b>1a</b>	Propan-2-ol	60	6	<b>2a</b>	84	70 <sup>c</sup>
2	<b>1a</b>	Butan-2-ol	80	6	<b>2a</b>	92	72 <sup>c</sup>
3 <sup>d</sup>	<b>1a</b>	Propan-2-ol	60	16	<b>2a</b>	88	71 <sup>c</sup>
4 <sup>e</sup>	<b>1a</b>	Propan-2-ol	60	24	<b>2a</b>	71	53 <sup>c</sup>
5	<b>1b</b>	Propan-2-ol	60	6	<b>2b</b>	— <sup>f</sup>	80 <sup>c</sup>
6	<b>1c</b>	Propan-2-ol	60	16	<b>2c</b>	100	74
7	<b>1d</b>	Propan-2-ol	60	6	<b>2d</b>	88	21
8	<b>1e</b>	Propan-2-ol	60	16	<b>2e</b>	89	71
9	<b>1f</b>	Propan-2-ol	60	16	<b>2f</b>	60	56
10	<b>1f</b>	Butan-2-ol	75	8	<b>2f</b>	89	78
11	<b>1g</b>	Propan-2-ol	60	16	<b>2g</b>	88	70
12	<b>1h</b>	Propan-2-ol	60	27	<b>2h</b>	100	71
13	<b>1i</b>	Propan-2-ol	60	6	<b>2i</b>	— <sup>f</sup>	46 <sup>c</sup>
14	<b>1i</b>	Propan-2-ol	60	48	<b>2i</b>	— <sup>f</sup>	61 <sup>c</sup>
15	<b>1i</b>	Butan-2-ol	75	12	<b>2i</b>	— <sup>f</sup>	75 <sup>c</sup>
16	<b>1j</b>	Propan-2-ol	60	6	<b>2j</b>	64	22
17	<b>1j</b>	Butan-2-ol	80	6	<b>2j</b>	95	26

<sup>a</sup> Reagents and conditions: Pd(OAc)<sub>2</sub> (0.05 mmol), alkene (1.0 mmol), pyridine (0.2 mmol), toluene (5 mL), alcohol (5 mL), O<sub>2</sub>. <sup>b</sup> Based on the amount of alkene employed. <sup>c</sup> GLC yield. <sup>d</sup> 2.5 mol% Pd(OAc)<sub>2</sub> and 10 mol% pyridine were used. <sup>e</sup> 1.0 mol% Pd(OAc)<sub>2</sub> and 4.0 mol% pyridine were used. <sup>f</sup> Not determined.

**Scheme 2** Plausible reaction pathway.

**Fig. 2** Time profile of the oxidation of dodec-1-ene: the relationship between O<sub>2</sub> uptake and product yield. The reaction was carried out on a 3 fold scale using propan-2-ol. O<sub>2</sub> uptake (□), produced dodecan-2-one (○), and O<sub>2</sub> uptake (△) in the reaction without dodec-1-ene.

species for the alkene oxidation in catalytic cycle B of Scheme 2.

## Conclusions

A novel system of the combination of Pd(OAc)<sub>2</sub>–pyridine–propan-2-ol–O<sub>2</sub> showed high catalytic activity in the selective

oxidation of terminal alkenes to methyl ketones. The *in situ* formation of H<sub>2</sub>O<sub>2</sub> in the oxidation of the alcohol is a key reaction. Although our system has some limitations as a synthetic method, these results present a new and mild catalytic cycle for the aerobic oxidation of terminal alkenes and strongly support the idea that a Pd(II)–OOH species is produced in the aerobic oxidation of alcohols as previously proposed.<sup>10b</sup>

## Experimental

### General

NMR spectra were recorded on JEOL EX-400 (<sup>1</sup>H NMR, 400 MHz; <sup>13</sup>C NMR, 100 MHz) and JNM-AL-300 (<sup>1</sup>H NMR, 300 MHz; <sup>13</sup>C NMR, 75.5 MHz) instruments for solutions in CDCl<sub>3</sub> with Me<sub>4</sub>Si as an internal standard: the following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, qui: quintet, m: multiplet. GLC analyses were performed on a Shimadzu GC-14A instrument (25 m × 0.33 mm, 5.0 mm film thickness, Shimadzu fused silica capillary column HiCap CBP10-S25-050) with flame-ionization detectors and helium as carrier gas. GLC yields were determined using bibenzyl as an internal standard. Analytical thin layer chromatography (TLC) was performed with Merck silica gel 60 F-254 plates. Column chromatography was performed with Merck silica gel 60.

## Materials

Commercially available organic and inorganic compounds were used without further purification except for the solvent, which was distilled by the known method before use. 5-*tert*-Butyldimethylsilyloxy-pent-1-ene (**1e**) was prepared by the reaction of pent-4-en-1-ol with *tert*-butyldimethylchlorosilane in the presence of imidazole in *N,N*-dimethylformamide. 5-Benzoyloxy-pent-1-ene (**1f**) was prepared by the reaction of pent-4-en-1-ol with benzoyl chloride in pyridine. 5-(Tetrahydropyran-2-yl)-pent-1-ene (**1g**) was prepared by the reaction of pent-4-en-1-ol with 3,4-dihydro-2*H*-pyran in the presence of K10 montmorillonite in CH<sub>2</sub>Cl<sub>2</sub>. 2-Allylcyclohexan-1-one (**1j**) was prepared by the enamine method.<sup>18</sup>

**5-*tert*-Butyldimethylsilyloxy-pent-1-ene (1e).** Colorless oil;  $\delta_{\text{H}}$ (300 MHz, CDCl<sub>3</sub>, CHCl<sub>3</sub>) 0.05 (6H, s), 0.90 (9H, s), 1.57–1.66 (2H, m), 2.07–2.14 (2H, m), 3.62 (2H, t,  $J = 6.4$  Hz), 4.93–5.05 (2H, m), 5.83 (1H, ddt,  $J = 17.1, 10.3, 6.6$  Hz);  $\delta_{\text{C}}$ (75.5 MHz, CDCl<sub>3</sub>, CHCl<sub>3</sub>) –5.3, 18.3, 26.0, 30.0, 32.0, 62.5, 114.5, 138.6.

**5-Benzoyloxy-pent-1-ene (1f).** Colorless oil;  $\delta_{\text{H}}$ (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 1.81–1.92 (2H, m), 2.16–2.26 (2H, m), 4.33 (2H, t,  $J = 6.6$  Hz), 4.97–5.05 (1H, m), 5.07 (1H, dq,  $J = 17.1, 1.7$  Hz), 5.85 (1H, ddt,  $J = 17.1, 10.3, 6.6$  Hz), 7.38–7.46 (2H, m), 7.50–7.58 (1H, m), 8.01–8.08 (2H, m);  $\delta_{\text{C}}$ (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 27.9, 30.2, 64.3, 115.4, 128.3, 129.6, 130.5, 132.8, 137.5, 166.6.

**5-(Tetrahydropyran-2-yl)pent-1-ene (1g).** Colorless oil;  $\delta_{\text{H}}$ (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 1.46–1.90 (8H, m), 2.09–2.18 (2H, m), 3.40 (1H, dt,  $J = 9.7, 6.6$  Hz), 3.45–3.55 (1H, m), 3.75 (1H, dt,  $J = 9.7, 6.6$  Hz), 3.82–3.92 (1H, m), 4.58 (1H, dd,  $J = 4.2, 2.8$  Hz), 4.90–5.01 (1H, m), 5.03 (1H, dq,  $J = 17.1, 1.7$  Hz), 5.83 (1H, ddt,  $J = 17.1, 10.3, 6.6$  Hz);  $\delta_{\text{C}}$ (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 19.7, 25.6, 29.1, 30.5, 30.8, 62.2, 66.9, 98.8, 114.7, 138.4.

## General procedure for palladium(II)-catalyzed oxidation of alk-1-ene to alkan-2-one using molecular oxygen

Pyridine (0.2 mmol) was added to a mixture of Pd(OAc)<sub>2</sub> (11.2 mg, 0.05 mmol) and toluene (5 mL) in a 20 mL two-necked flask equipped with an O<sub>2</sub> balloon. Oxygen gas was introduced into the flask and propan-2-ol (1 mL) was added at 60 °C. The yellow solution turned to yellowish orange when the propan-2-ol was added. After the reaction had been left at 60 °C for ca. 5 min, the appropriate alk-1-ene (1 mmol) in propan-2-ol (4 mL) was added and the mixture was stirred for 6 h at 60 °C under O<sub>2</sub>. The reaction mixture was passed through Florisil, and the amount of the corresponding product was determined by GLC analysis (for **2a**, **2b** and **2i**) using bibenzyl as an internal standard. In the case of compounds **2c–h** and **2j** the solvent was first evaporated and the residue was then purified by column chromatography on silica gel using hexane and ethyl acetate as eluents.

**5-*tert*-Butyldimethylsilyloxy-pent-2-one (2e).** Colorless oil;  $\delta_{\text{H}}$ (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 0.03 (6H, s), 0.87 (9H, s), 1.77 (2H, qui,  $J = 6.7$  Hz), 2.14 (3H, s), 2.50 (2H, t,  $J = 6.7$  Hz), 3.60 (2H, d,  $J = 6.7$  Hz);  $\delta_{\text{C}}$ (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) –5.5, 18.2, 25.8, 26.8, 29.8, 40.0, 62.0, 208.7.

**5-Benzoyloxy-pent-2-one (2f).** White solid, mp 45.2–47.0 °C;  $\delta_{\text{H}}$ (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 2.06 (2H, qui,  $J = 6.7$  Hz), 2.17 (3H, s), 2.61 (2H, t,  $J = 6.7$  Hz), 4.33 (2H, t,  $J = 6.7$  Hz), 7.38–7.60 (3H, m), 8.03 (2H, d,  $J = 7.7$  Hz);  $\delta_{\text{C}}$ (75.5 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 22.9, 30.0, 39.9, 64.1, 128.4, 129.5, 130.2, 133.0, 166.5, 207.6.

**5-(Tetrahydropyran-2-yl)pent-2-one (2g).** Colorless oil;  $\delta_{\text{H}}$ (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 1.35–1.85 (8H, m), 2.09 (3H, s),

2.47 (2H, t,  $J = 7.2$  Hz), 3.33 (1H, dt,  $J = 9.7, 6.1$  Hz), 3.37–3.46 (1H, m), 3.67 (1H, dt,  $J = 9.7, 6.1$  Hz), 3.70–3.83 (1H, m), 4.48 (1H, br s);  $\delta_{\text{C}}$ (75.5 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 19.7, 24.0, 25.5, 29.9, 30.7, 40.6, 62.4, 66.5, 98.9, 208.6.

**11-Hydroxyundecan-2-one (2h).** White solid, mp 38.5–39.7 °C;  $\delta_{\text{H}}$ (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 1.25–1.58 (15H, m), 2.14 (3H, s), 2.42 (2H, t,  $J = 7.3$  Hz), 3.64 (2H, t,  $J = 6.6$  Hz);  $\delta_{\text{C}}$ (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 23.8, 25.7, 29.2, 29.3, 29.4, 29.4, 29.9, 32.8, 43.8, 63.0, 209.5.

## Acknowledgements

The author T. N. is grateful for the award of a Fellowship of the Japan Society for the Promotion of Science for Young Scientists.

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- Another product was detected by TLC analysis, but it could not be isolated due to its high volatility. <sup>1</sup>H NMR of the crude reaction mixture did not show any signals due to the aldehyde proton in low field, suggesting that the oxidation of the hydroxy group in **1d** may be slower than that of a terminal alkene.
- The oxidation of **1h** using Pd(OAc)<sub>2</sub>–pyridine–3 Å molecular sieve–O<sub>2</sub> catalytic system yielded undec-10-en-1-al in 91% yield after 17 h; unpublished results.
- We examined the oxidation of **1i** using Mimoun's method (Pd(OAc)<sub>2</sub> and 30% H<sub>2</sub>O<sub>2</sub>), but overoxidation proceeded to give acetophenone as a major product. In our present system, the formation of acetophenone was not observed.
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