Palladium-Catalyzed Oxidation of Dihydromyrcene to Citronellal in Supercritical Carbon Dioxide

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Citronellal was the major product of catalytic oxidation of dihydromyrcene with oxygen using the catalyst comprised of $(MeCN)_2PdClNO_2$ and $CuCl_2$ in a tertiary alcohol in supercritical carbon dioxide. It was found that the chemoselectivity of the reaction and the yield of citronellal were greatly affected by the pressure of carbon dioxide, the reaction temperature and the molar ratio of Pd/Cu.

Keywords supercritical carbon dioxide, dihydromyrcene, Pd-catalyzed, oxidation reaction, citronellal

Selective catalytic oxidation reaction of terminal alkenes with molecular oxygen was commercially important processes affording aldehydes and methyl ketones. A considerable number of studies have been made on these reactions.[1] But the selectivity to aldehydes was usually poor in those reactions. In previous work, we found that palladium-catalyzed radical co-addition reaction of terminal alkenes had good yield and conversion in supercritical carbon dioxide ($scCO_2$).[2] Now we wish to report the modified palladium (II)-nitro complex as catalyst for the oxidation of dihydromyrcene to citronellal with good yield and selectivity in $scCO_2$. It was noted that not only radical reaction was one of the successful examples to employ $scCO_2$ as the reaction medium, but also the oxidation reaction was another nice example (Scheme 1).

Scheme 1
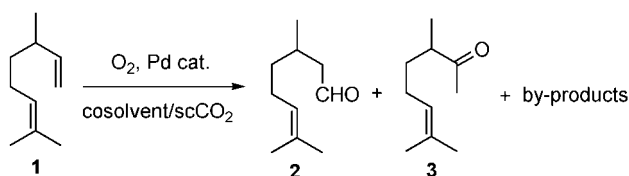
The preliminary studies revealed that the pressure of carbon dioxide, reaction temperature and molar ratio of $(MeCN)_2PdClNO_2$ to $CuCl_2$ influenced the selectivity to citronellal. The most satisfying results were obtained at 10 MPa of CO_2 (Table 1, Entries 7—9). Also it

was found that the optimum temperature was 80 ℃ (Table 1, Entries 6, 7). Although the conversion rose to 96% (or 97%) (Table 1, Entries 8, 9) at higher temperature, the selectivity to citronellal dropped down to 83% (or 81%). Moreover the selectivity depended on molar ratio of $(MeCN)_2PdClNO_2$ to $CuCl_2$ (Entries 14, 15). The results of oxidation of dihydromyrcene in $scCO_2$ under the different reaction conditions are summarized in Table 1.

As shown in Table 1, the longer the reaction time, the higher the conversion and the lower the selectivity to citronellal (Entry 11). Also the pressure of oxygen had less effect on the conversion of dihydromyrcene and the selectivity to citronellal (Entry 12). On the contrary, the selectivity dropped down to 13% (Entry 13), when EtOH was used instead of *t*-BuOH.

The possible mechanism interpretation of citronellal formation involved an oxygen transformation reaction via initial cyclo-addition of nitro-palladium complex **a** leading to five-membered ring intermediate **b**, followed by the *β*-hydrogen elimination in the metallocycle. The Cu^{II} salts and *t*-BuOH played a key role on the selectivity to citronellal. They combined with $(MeCN)_2$-PdClNO_2 giving hindered nucleophilic reagent **a**, which apparently behaved as a hindered nucleophile that attacked at the less-hindered terminal carbon carbon double bond of dihydromyrcene. And this process did not involve the internal carbon carbon double bond of dihydromyrcene due to the steric restriction masks, as shown in Scheme 2.[3]

**Table 1** Oxidation reaction of dihydromyrcene to citronellal in scCO$_2$

Entry	p(CO$_2$)/ MPa	Temp./°C	Conv.^{a}/%	Yield^b/%		Selectivity/% [**1**/(**1**+**2**)]
				1	**2**	
1	—	60	45	30	20	60
2	5	60	48	32	13	71
3	6	65	52	30	16	65
4	7	70	50	32	14	70
5	8	75	68	58	13	82
6	9	80	92	57	12	83
7	10	80	95	79	13	86
8	10	85	96	74	15	83
9	10	90	97	68	16	81
10	12	80	92	77	17	82
11^c	10	80	98	60	20	75
12^d	10	80	95	78	16	83
13^e	10	80	65	10	70	13
14^f	10	80	90	75	17	82
15^g	10	80	91	70	13	84
16^h	10	80	90	25	73	26
17^i	10	80	92	2	95	2
18^j	10	80	95	78	13	85

^{a} Reaction conditions: dihydromyrcene (2 mmol), O$_2$ (2 MPa), CO$_2$ (the desired pressure), (MeCN)$_2$PdClNO$_2$ (0.01 mmol), CuCl$_2$ (0.05 mmol) and t-BuOH (1 mL) reacted for 10 h in a 10 mL stainless steel autoclave. ^{b} Determined by GC analysis. ^{c} Reacted for 24 h. ^{d} Reacted under 4 MPa of O$_2$. ^{e} EtOH was used instead of t-BuOH. ^{f} The molar ratio of (MeCN)$_2$PdClNO$_2$/CuCl$_2$ =1/3. ^{g} The molar ratio of (MeCN)$_2$- PdClNO$_2$/CuCl$_2$=1/5. ^{h} (MeCN)$_2$PdCl$_2$ (0.01 mmol) was used instead of (MeCN)$_2$- PdClNO$_2$. ^{i} (MeCN)$_2$PdClNO$_2$ was substituted by PdCl$_2$ (0.01 mmol). ^{j}The molar ratio of (MeCN)$_2$- PdClNO$_2$/CuCl=1/3.

Scheme 2

L=MeCN-CuCl$_2$-Me$_3$COH
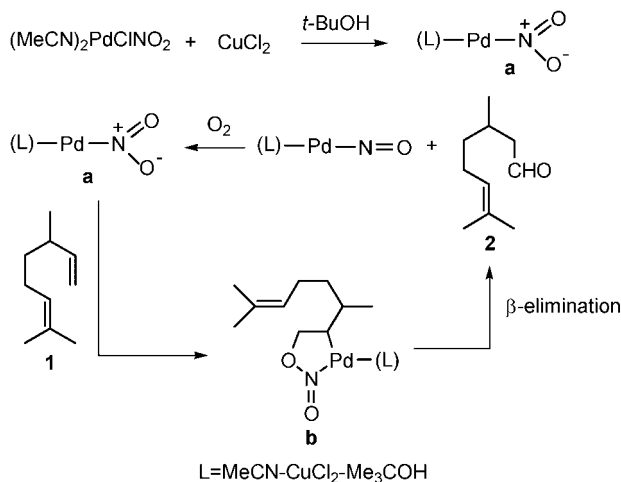
To verify this mechanism, we conducted contrast experiments as follows: when (MeCN)$_2$PdCl$_2$ was used instead of (MeCN)$_2$PdClNO$_2$, it was found that the selectivity to citronellal was greatly decreased (Entry 16). Moreover, only trace citronellal was found, if PdCl$_2$ was used instead of (MeCN)$_2$PdClNO$_2$ (Entry 17). Both selectivity and conversion remained constant as CuCl$_2$ was substituted by CuCl (Entry 18).

Our studies showed that the selectivity to citronellal and conversion of dihydromyrcene were effectively controlled by scCO$_2$ as the reaction medium. Also it demonstrated the fact that the oxidation could be conducted in scCO$_2$.

This heterogeneous catalytic oxidation system comprised three phases: solid [(MeCN)$_2$PdClNO$_2$], liquid (dihydromyrcene) and gas (O$_2$). Oxygen was well diffused in scCO$_2$.[4] Still the reactants such as dihydromyrcene, t-BuOH, (MeCN)$_2$PdClNO$_2$ and CuCl$_2$ were miscible in scCO$_2$,[5] because scCO$_2$ had good solvability.[6] As a result, the system was changed into homogeneous reaction, and the selectivity to citronellal and conversion of dihydromyrcene were good in supercritical carbon dioxide reaction medium.

Experimental

IR spectra were gained with a WQF-410 FTIR spectrometer. ^{1}H NMR spectra were taken on a 400 MHz spectrometer with tetramethylsilane as the internal standard and CDCl$_3$ as the solvent. GC data were obtained by a VARIAN 3700GC instrument. MS spectra were recorded on an HP 6890-5973 MS spectrometer. Dihydromyrcene (Guangxi Wuzhou Pine Chemicals Ltd, GC analysis 95%), (MeCN)$_2$PdClNO$_2$ (Allied Chemical Corporation, analytical grade). Other reagents employed were of analytical grade and commercially available.

General procedure

(MeCN)$_2$PdClNO$_2$ (0.01 mmol), CuCl$_2$ (0.05 mmol), and t-BuOH (1 mL) were added to a 10 mL stainless steel autoclave and reacted for 1 h at reaction temperature 50 °C. Then dihydromyrcene (2 mmol) added, O$_2$ (2 MPa) and CO$_2$ (the desired pressure) was charged in this reaction system. The reaction was carried out at appointed temperature and pressure for 10 h. After venting O$_2$ and removing the metal species and solvent, the products were purified by column chromatography on silica gel (8 : 1 hexane-ether) and then was determined by ^{1}H NMR (400 MHz) and GC (quantitative analysis) .

Citronellal (2): ^{1}H NMR (CDCl$_3$/TMS, 400 MHz) δ: 0.94 (d, J=6.8 Hz, 3H, CH$_3$), 1.20—1.40 (m, 4H, 2CH$_2$), 1.57 (s, 3H, CH$_3$), 1.66 (s, 3H, CH$_3$), 2.15—2.30 (m, 1H, CH), 2.40 (d, J=5.6 Hz, 2H, CH$_2$), 5.00—5.10 (m, 1H, =CH), 9.73 (s, 1H, —CHO); IR (film) v: 1728 (HC=O), 3020 (=C—H), 2964, 2919, 2915 (CH$_3$), 1654 (C=C) cm^{-1}; MS (70 eV) m/z (%): 154, 139, 121, 95, 69.

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3,7-Dimethyl-6-octen-2-one (3): ^{1}H NMR (CDCl$_3$/TMS, 400 MHz) δ: 1.01 (d, J=6.9 Hz, 3H, CH$_3$), 1.20—1.30 (m, 2H, CH$_2$), 1.52 (s, 3H, CH$_3$), 1.63 (s, 3H, CH$_3$), 1.88 (q-like, J=7.6 Hz, 2H, CH$_2$), 2.06 (s, 3H, CH$_3$), 2.20—2.35 (m, 1H, CH), 5.10 (tt-like, J=1.3, 7.1 Hz, 1H, =CH); IR (film) v: 1720 (C=O), 3020 (=C—H), 2950, 2910 (CH$_3$), 1640 (C=C) cm^{-1}; MS (70 eV) m/z (%): 154, 139, 128, 108, 69.

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