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Preliminary communication

A palladium(II) catalyst for oxygenation of terminal olefins with molecular oxygen

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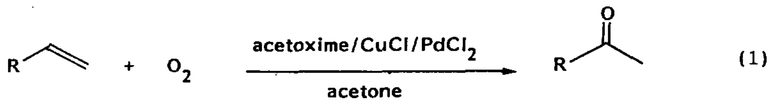
Abstract

Oxidation of terminal olefins with molecular oxygen by a catalyst system consisting of acetoxime, CuCl, and $PdCl_2$ in anhydrous acetone gives the corresponding methyl ketones.

The transition-metal-catalyzed oxidation of hydrocarbons with molecular oxygen has recently attracted considerable attention from both synthetic and mechanistic viewpoints [1]. Most of the work in this area has been directed towards the development of non-free-radical oxidations of alkenes [2]. We report here that this type of oxidation is achieved by a novel catalytic system consising of acetoxime, CuCl, and $PdCl_2$ in a non-aqueous solution (eq. 1).



The typical procedure for the oxidation of dec-1-ene (**1**) to decan-2-one (**2**) is described as follows. To a dark-green solution (prepared from CuCl (2 mmol) and acetoxime (2 mmol) in anhydrous acetone (5 ml) by stirring at room temperature for 2 h under O_2 (1 atm, balloon)) was added $PdCl_2$ (1 mmol), and the resulting mixture was stirred at 50 °C for 22 h. A solution of **1** (10 mmol) in anhydrous acetone (3 ml) was then added dropwise over a period of ca. 3–7 h under O_2 (1 atm). The mixture was further stirred for 21 h, ether was added, and the residue filtered off. Evaporation of the filtrate, followed by column chromatography (SiO_2, CH_2Cl_2) gave **2** in 560–700% yield (based on Pd). The yield of **2** is dependent on the rate of addition of **1** to the catalyst system. If a solution of **1** is added in one portion, the yield is reduced to 330%. In the absence of either CuCl or acetoxime, virtually no reaction takes place.

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Table 1

Oxygenation of olefins [a]

Entry	Olefins	Oxidized products (yield (%)) [b]
1	$CH_3(CH_2)_7CH{=}CH_2$ (**1**)	$CH_3(CH_2)_7COCH_3$ (**2**) (560–700)
2	$CH_3(CH_2)_{11}CH{=}CH_2$	$CH_3(CH_2)_{11}COCH_3$ (404)
3	$EtOOC(CH_2)_8CH{=}CH_2$	$EtOOC(CH_2)_8COCH_3$ (348)
4	$MeCOCH{=}CH(CH_2)_8CH{=}CH_2$	$MeCOCH{=}CH(CH_2)_8COCH_3$ (296)
5	$MeCO(CH_2)_2CH{=}CH_2$	$MeCO(CH_2)_2COCH_3$ (263)
6	$PhOCH_2CH{=}CH_2$	$PhOCH_2COCH_3$ (229) PhOH (191)
7	$PhCH{=}CH_2$	$PhCOCH_3$ (104) $PhCH_2CHO$ (5) PhCHO (145)

[a] The reaction conditions are shown in the text. [b] Isolated yield based on Pd.

With the catalytic system, terminal olefins such as those shown in Table 1 generally afford the corresponding methyl ketones. No straightforward result is obtained with styrene.

Although the catalytic system is apparently similar to that of the Wacker process, the present oxidation does not proceed via the Wacker reaction. This was comfirmed, when the oxidation of **1** was carried out in acetone containing $H_2{}^{18}O$ (3–5 equiv. per Pd), the ^{18}O content in **2** formed was negligible (1–5%) (Table 2). Further, the presence of water (3–55 equiv. per Pd) has little effect on the reaction. No radical process seems to be involved, since the presence of radical inhibitors, e.g. 2,6-di-t-butyl-4-methylphenol (1–0.1 equiv. per Pd), had no significant effect.

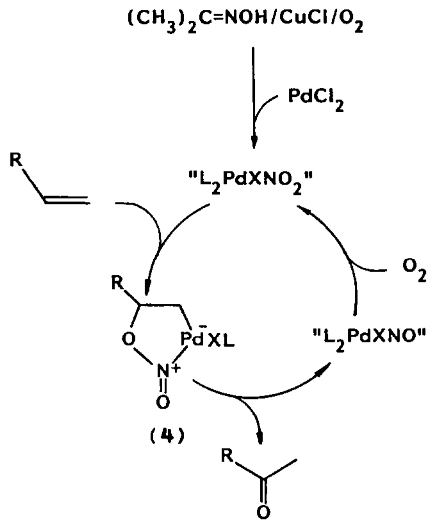
When heptan-4-one oxime was used in place of acetoxime under the aforementioned conditions ($CuCl : oxime : PdCl_2 = 2:2:1$), decan-2-one (**2**) was similarly obtained from **1** in 397% yield (based on Pd). In addition, 86% of the oxime charged was deoximated to given heptan-4-one during the step of the catalyst preparation. The deoximation was induced only by the action of CuCl and O_2, but its extent was not very high (23%). Upon addition of $PdCl_2$, the deoximation was accelerated and went to completion. Previously, we reported the deoximation of oximes with molecular oxygen in the presence of $Pd(PPh_3)_4$ [3]. In the present case, the oximino

Table 2

Oxidation of dec-1-ene (**1**) in acetone containing $H_2{}^{18}O$ [a]

Entry	$H_2{}^{18}O$ (equiv. per Pd)	Decan-2-one (**2**) Isolated yield (% based on Pd)	^{18}O-content [b] (%)
1	0	564	–
2	3.0 [c]	455	5
3	5.0 [d]	320	1

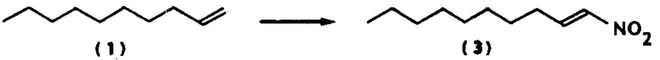
[a] Conditions: acetoxime (0.4 mmol), CuCl (0.4 mmol), $PdCl_2$ (0.02 mmol), **1** (2 mmol), acetone (2 ml), $H_2{}^{18}O$ (12–20 μl), time required for dropwise addition of **1** is ca. 3 h. [b] GC-MASS (Shimazu QP-1000) analysis. [c] 58% $H_2{}^{18}O$ was used. [d] 98% $H_2{}^{18}O$ (CEA-ORIS) was used.



SCHEME 1. Oxygenation process of olefins, where X = Cl or NO$_2$.

group (>C=NOH) is thought to be converted into a NO$_2$ ligand of Pd^{II} by the following:

When a large amount of CuCl and acetoxime (20 equiv. per Pd) was employed in dimethoxythane (DME) solvent, (*E*)-1-nitrodec-1-ene (3) was obtained from **1** as the major product (252% GLC yield based on Pd) together with **2** (176%) (eq. 2).



(1) (3) + 2 (2)

The spectral and analytical data of **3** are as follows: R_f 0.14 (SiO$_2$, benzene/hexane = 2/8); ^{1}H NMR (CCl$_4$) δ 0.90 (bt, 3H, CH$_3$), 1.30 (m, 12H, CH$_2$), 2.21 (bt, 2H, CH$_2$C=), 6.83 (d, J 14 Hz, 1H, =CHNO$_2$), 7.17 (dt, J 14 and 7 Hz, 1H, CH=); IR (neat) 1658, 1524, 1350, 962, 861, 724 cm^{-1}; Anal. Found: C, 64.91; H, 10.30; N, 7.22. C$_{10}$H$_{19}$O$_2$N calc: C, 64.83; H, 10.34; N, 7.56%. Interestingly the regioselectivity of this nitration is reversed compared to the reaction of the dinitro complex of (CH$_3$CN)$_2$Pd(NO$_2$)$_2$ [4]. The nitroalkene seems to be formed by nitropalladation involving a NO$_2^-$ ion that has dissociated from the metal, followed by Pd–H elimination.

The present oxidation is thus rationalized by the pathway involving PdXNO$_2$ species (X = Cl or NO$_2$) leading to the cyclic intermediate (4) [5–9] as shown in Scheme 1. The nitro complex, (CH$_3$CN)$_2$PdClNO$_2$, which is prepared from (CH$_3$CN)$_2$PdCl$_2$ and AgNO$_2$, has been shown to effect catalytic oxidation of **1** to **2** in 375% yield [5]. In contrast, our procedure appears to be preferable in terms of high catalytic turnover, and there is no need for the expensive silver salt. Although details of the present system are still unclear, it has valuable implications in that oximes could be utilized as the source of NO$_2$ ligand for metal catalysts.

References

1 R.A. Sheldon and J.K. Kochi, 'Metal-Catalyzed Oxidations of Organic Compounds,' Academic Press, New York, 1981.

2 I. Ingersheim and H. Mimoun, Nouv. J. Chim., 4 (1980) 161; R.S. Drago, A. Zuzich, and E.D. Nyberg, J. Am. Chem. Soc., 107 (1985) 2898, and references cited therein.
3 K. Maeda, I. Moritani, T. Hosokawa, and S.-I. Murahashi, Tetrahedron Lett, (1974) 797.
4 M.A. Andrews, T.C.-T. Chang, C-W.F. Cheng, L.V. Kapustay, K.P. Kelly, and M.J. Zweifel, Organometallics, 3 (1984) 1479.
5 M.A. Andrews, T.C.-T. Chang, C-W.F. Cheng, and K.P. Kelly, Organometallics, 3 (1984) 1777.
6 M.A. Andrews, T.C.-T. Chang, and C-W.F. Cheng, Organometallics, 4 (1985) 268.
7 F. Mares, S.E. Diamond, F.J. Regina, and J.P. Solar, J. Am. Chem. Soc., 107 (1985) 3545.
8 A. Heumann, F. Chauvet, and B. Waegell, Tetrahedron Lett., 23 (1982) 2767.
9 B.L. Ferigna, J. Chem. Soc., Chem. Commun., (1986) 606.