MULTI-STEP CATALYSIS FOR THE OXIDATION OF OLEFINS TO KETONES BY MOLECULAR OXYGEN IN CHLORIDE FREE MEDIA

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Summary: A multi-step catalytic system consisting of Pd(II)/Pd(0) - benzoquinone/hydroquinone - $Fe(Pc)_{ox}/Fe(Pc)$ was utilized to achieve a mild and selective aerobic oxidation of terminal olefins to methyl ketones in chloride free media.

A number of processes for metal-catalyzed oxidations of olefins to ketones by molecular oxygen are known in the literature.¹⁻⁶ Most of these procedures show a high selectivity but proceed at a moderate rate at room temperature. Several require elevated temperature and oxygen pressure. Of particular interest is the palladium-catalyzed oxidation of ethene to acetaldehyde (the Wacker Process)^{1,2} and its extension to terminal long chained olefins (eq. 1),³ which is a useful synthetic method for the preparation of methyl ketones.⁴

A drawback with the presence of cupric chloride and chloride ions, however, is that the reaction proceeds at a moderate rate⁷ and furthermore, chlorination side products are often formed.⁸ A chloride free Wacker oxidation would therefore be highly desirable. We report here a mild and selective procedure for the oxidation of terminal olefins by molecular oxygen in the absence of chloride ligands.

The palladium-catalyzed oxidation of terminal olefins using a stoichiometric amount of p-benzoquinone as oxidant has previously been described.^{3a} We have recently developed a catalytic system for the reoxidation of hydroquinone to p-benzoquinone by molecular oxygen utilizing a macrocyclic metal complex as catalyst.⁹ We therefore sought to develop a new Wacker system for the rapid oxidation of higher olefins employing a well defined multi-step catalytic system based on a palladium salt, p-benzoquinone and an oxygen-activating transition metal complex.

Initial attempts to develop a chloride free system using $Pd(OAc)_2$ with hydroquinone and an oxygen activating complex in aqueous DMF (*N*,*N*-dimethylformamide) failed due to the almost immediate precipitation of metallic palladium from the reaction mixture. The addition of a small amount (5-15 mol%) of a strong acid prevents the precipitation of Pd⁰. This is probably due to the protonation of an otherwise labile Pd⁰-olefin

 $complex^{10}$ or to the promotion of the oxidation of Pd^0 by benzoquinone via protonation of the benzoquinone. This modification has led to a rapid catalytic system capable of multiple turnovers in the selective oxidation of higher 1-olefins to the corresponding 2-ketones.

The selection of an oxygen activating complex for the recycling of hydroquinone to *p*-benzoquinone demanded particular attention. The presence of the strong acid along with H_2O requires that the complex not be sensitive to acid promoted hydrolysis. This eliminates the use of Schiff's base complexes such as Co(salen) under the reaction conditions. It was shown that the reaction died quickly when Co(salen) was used as the oxygen carrier. Attempts to employ Co(TPP) as oxygen activator also led to poor results. The reaction, as monitored by the O_2 uptake, was initially rapid, but ceased before complete conversion of the olefin. Thin-layer chromatographic analysis of the resultant reaction mixture revealed decomposition of the porphyrin.



The best results have been obtained with iron phthalocyanine (Fe(Pc)) as the oxygen activating species. Reports in the literature of the use of Fe(Pc) for the activation of molecular oxygen are found as early as 1938,¹¹ but little has been done to develop this to a useful degree. An attractive attribute of Fe(Pc) is its high chemical stability. This stability is due in part to its insolubility in most organic solvents so that, at the end of the reaction, most of it may be recovered via filtration. In the reaction system with 5% (molar % relative to olefin) Pd(OAc)₂, 15% hydroquinone, 5% HClO₄, and 5% Fe(Pc) in aqueous DMF, yields of 73% of 2-decanone from 1-decene are consistently obtained after three hours at room temperature (eq. 2). After this time 100% conversion of the olefin to the methyl ketone and a mixture of isomerized olefins has occured.



Increasing the concentration of acid has no major effect on the overall rate, but does increase the amount of olefin isomerization. With no acid, Pd metal rapidly precipitates from the reaction mixture. If the hydroquinone is omitted the reaction does proceed at a slow rate, but not to completion. The rate increases significantly when hydroquinone is added up to 7% relative to olefin concentration. Increasing the hydroquinone concentration to 15% does not further increase the rate, but does lead to an increase in the yield of 2-ketone. Several other terminal olefins were tested and oxidized to their corresponding methyl ketones by this method. Table 1 summarizes the results of these trials.

entry	olefin	reaction time (h)	product ^b	% yield ^c
1	$CH_3(CH_2)_7CH = CH_2$	3	CH ₃ (CH ₂) ₇ COCH ₃	73
2	$CH_3(CH_2)_9CH = CH_2$	8	CH ₃ (CH ₂) ₉ COCH ₃	67
3	Ů	2	ů v v	85
4	\bigcirc	5	Q°,Ľ	47 ^d
5	OEt	8		82

Table 1 Aerobic oxidation of terminal olefins via multi-step catalysis[®]

a. All reactions were performed in aqueous DMF (DMF : $H_2O = 89 : 11$) at 20°C under an atmospheric pressure of oxygen using 5 mol % of Pd(OAc)₂, 5 mol % of Fe(Pc) and 15 mol % of hydroquinone. The olefin was added in portions during 1-2 h. b. The products were characterized by ¹H and ¹³C NMR spectroscopy. The only oxidized product detected were the ketones shown (> 98 % selectivity) c. Isolated yields after flash chromatography d. Decomposition of the starting material to phenol occured in this case.

In a typical experiment a two neck 10 ml round-bottom flask equipped with a magnetic stir bar and septum in one neck was charged with Pd(OAc)₂ (0.017 g, 0.076 mmol), hydroquinone (0.025 g, 0.23 mmol), iron phthalocyanine (0.043 g, 0.076 mmol) and 1.0 ml distilled *N*,*N*-dimethylformamide. To this was added via syringe 0.12 ml H₂O and 8 μ l of 60% aqueous HClO₄ (0.076 mmol). The reaction vessel was carefully purged with O₂ with three pump-fill cycles (water aspirator vacuum) and 1-decene (0.21 g, 1.5 mmol) was added in six portions at 15 minute intervals. The mixture was stirred at room temperature under 1 atm O₂ and the O₂ uptake measured with a burette. After 3 h (17.5 ml O₂ consumed) the reaction mixture was diluted to 15 ml with brine solution and extracted with 2 x 20 ml pentane and once with 20 ml pentane/ether (85:15) and the organic phases dried over anhydrous Na₂SO₄. Gas chromatographic analysis of the combined extracts gave a 78% yield of ketone. The remaining olefin and ketone were separated by column chromatography over silica with pentane followed by pentane/ether (gradient up to 85:15) to give an isolated yield of 171 mg (73%) of 2-decanone. ¹H NMR analysis indicated only decane-2-one as the oxidized product. ¹H and ¹³C NMR analyses of the remaining olefin indicated a mixture of olefin isomerization products.

As a control, the reaction of 1-decene was run with a stoichiometric amount of p-benzoquinone as the oxidant. This particular reaction has been reported previously by Clement and Selwitz^{3a} using $PdCl_2$ (20%) in DMF at 70 °C for three hours to give a 77% yield of 2-decanone. In our hands, with 5% $Pd(OAc)_2$ in aqueous DMF and the addition of 10% $HClO_4$, a yield of 92% of 2-decanone was obtained after two hours at room temperature. This procedure, though not employing molecular oxygen, may be of interest for the laboratory scale preparation of methyl ketones from terminal olefins under very mild conditions.

The mechanism of the chloride-free Wacker-type oxidation developed proceeds via a multi-step catalysis (Scheme 1). Such triple catalysis has been illustrated previously in the palladium-catalyzed oxidation of conjugated dienes.^{9,12} A related process for the oxidation of olefins to ketones in which hydroquinone was reoxidized electrochemically was recently reported.¹³

Scheme 1



The coupling of the palladium catalyzed oxidation of terminal olefins to a new oxygen activating system effecting a multistep catalytic process has led to a faster, more efficient reaction giving high yields under mild conditions. Further efforts to improve the yields and rates, and to extend the scope of this process are currently underway in these laboratories.

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