Tetrahedron Letters,Vol.28,No.32,pp 3683-3686,1987	0040-4039/87 $3.00 + .00
Printed in Great Britain	Pergamon Journals Ltd.

OXIDATION OF OLEFINS TO KETONES IN COMBINATION WITH ELECTROOXIDATION

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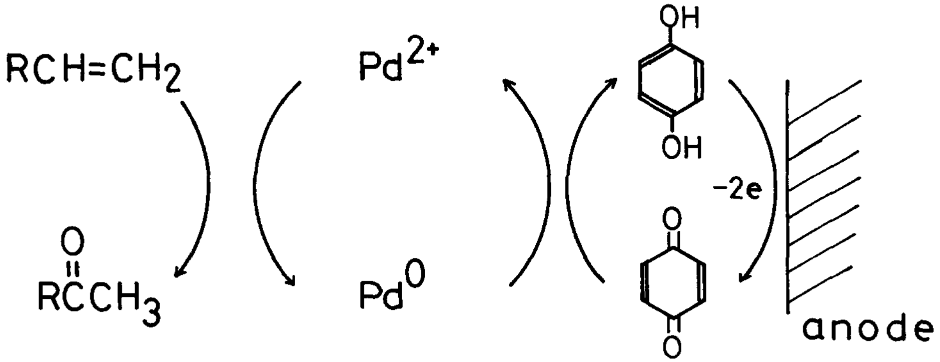
SUMMARY: In combination with anodic oxidation, 1-alkenes are oxidized to methyl ketones efficiently by the catalyses of $Pd(OAc)_2$ and benzoquinone. Cyclopentene and Cyclohexene are oxidized smoothly to the corresponding ketones in high yields.

Oxidation of 1-alkenes to methyl ketones with Pd^{2+}salts is well-established synthetic method.[1-4] In this oxidation, Pd^{2+} is reduced to Pd^0, and some appropriate reoxidants which can oxidize Pd^0 to Pd^{2+} must be used to make the reaction catalytic with respect to palladium. Inorganic salts such as $CuCl_2$, CuCl, MnO_2, $FeCl_3$, and heteropoly acid are used for this purpose. Among them, copper salts are used commonly under oxygen atmosphere and the reaction is catalytic with respect to both palladium and copper salts. However one drawback of the $PdCl_2/CuCl_2(orCuCl)/O_2$ system is that the reaction medium is not completely homogeneous when the reaction is carried out in aqueous DMF, and rather large amounts of Pd^{2+} and copper salts must be used, particularly for the oxidation of higer 1-alkenes. Sometimes nearly a stoichiometric amount of copper salts is necessary to complete the oxidation. On the other hand, efficient homogeneous oxidation is possible with a stoichiometric amount of organic oxidants such as benzoquinone[5-7] or peroxides.[8,9] A good oxidant of Pd^0 is benzoquinone, which is reduced to hydroquinone. It is well-known that hydroquinone can be oxidized easily to benzoquinone electrochemically.[10] Based on these facts, we attempted the oxidation of olefins with a catalytic system of $Pd(OAc)_2$ and benzoquinone, combined with electrochemical oxidation as expressed by the following diagram, and the results are presented in this communication.[11]



At first we carried out the oxidation of 1-decene to 2-decanone at room temperature under various conditions in order to find optimum conditions. Selection of solvent is most important, and a number of aqueous solvents such as CH_3CN, DMF, NMP (N-Methylpyrrolidinone), DMSO, DMI (1,3-Dimethyl-2-imidzolidinone), and AcOH were tested. The best results were obtained in CH_3CN, DMSO, and NMP as shown in Table 1. Then several supporting electrolytes were used as shown in Table 2. The oxidation can be carried out satisfactorily with 2 mol% of $Pd(OAc)_2$ and 20 mol% of benzoquinone.

Table 1. Solvent effect on the oxidation of 1-decene to 2-decanone using $Pd(OAc)_2$ and electrochemically regenerated benzoquinone.

Run	Solvent	Ratio to water	Yield[a)] %
1	CH_3CN	7 : 1	63
2	DMF	7 : 1	51
3	AcOH	1 : 1	13
4	NMP	7 : 1	60
5	DMSO	7 : 1	63
6	DMI	7 : 1	40

a) Determined by GLC using internal standard.

Table 2. Influence of the supporting electrolyte on the oxidation of 1-decene to 2-decanone.

Run	Supporting electrolyte	Yield[a)] %	Current yield %	Charge passed
7	Et_4NBF_4	63	48	18 mF
8	$NaBF_4$	66	51	18 "
9	nBu_4NClO_4	68	53	18 "
10	HBF_4[b)]	79	59	20 "

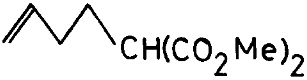
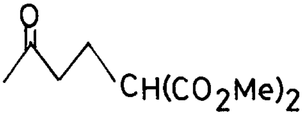
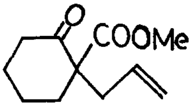
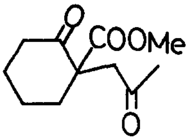
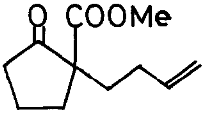
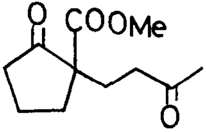
a) Determined by GLC using an internal standard.

b) Anolyte was prepared from DMSO (70 ml), and HBF_4 (10 ml, 35 % aqueous soln.).

Typical procedure is as follows. An anodic solution(50 ml) containing 1-decene (1.403 g, 10 mmol), benzoquinone (0.216 g, 2 mmol), $Pd(OAc)_2$ (0.0449 g, 0.2 mmol), and supporting electrolyte (Et_4NBF_4, 0.3 M) was electrolyzed using a Pt anode at 0.83 A dm^{-2} of a constant current density in a divided cell at room temperature. After passing 18 mF of charge, usual work-up provided 2-decanone.

Then we carried out the oxidation of several functionalized olefins and the results are shown in Table 3.

Table 3. Oxidation of olefins using $Pd(OAc)_2$, and electrochemically regenerated benzoquinone.[a]

Substrates	Solvents	Products	Yield[b] %
Styrene	DMSO	Acetophenone	56
Cyclopentene	CH_3CN	Cyclopentanone	75
Cyclohexene	CH_3CN	Cyclohexanone	83[c]
	DMSO		75[d][e]
	DMSO		69[d][e]
	DMSO		82[d][e]
	DMSO		76[d][e]

a) All electrolyses were carried out in the presence of $Pd(OAc)_2$(2 mol%), and benzoquinone(20 mol%) in aqueous solvent (solvent : water = 7 : 1) at room temperature.

b) Determined by GLC using an internal standard.

c) Electrolysis was carried out in the presence of $Pd(OAc)_2$(5 mol%) and benzoquinone(30 mol%).

d) Electrolysis was carried out in the presence of $Pd(OAc)_2$(4 mol%) and benzoquinone(20 mol%).

e) Isolated yield.

The oxidation proceeded smoothly in all cases. Particularly we were surprised to find that cyclopentene and cyclohexene were oxidized smoothly to give the corresponding cyclic ketones in good yields. It is known that the oxidation of these cyclic olefins with $PdCl_2/CuCl_2/O_2$ in organic solvents is extremely difficult.[12-14] For comparison, we attempted the oxidation of cyclohexene in aqueous CH_3CN using a catalytic amount of $Pd(OAc)_2$(5 mol%) and stoichiometric amount of benzoquinone without electrooxidation. But almost no oxidation took place. At present, it is somewhat difficult to explain why smooth oxidation of cyclohexene and cyclopentene proceeded smoothly under the electrooxidation conditions.

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(Received in Japan 6 April 1987)