

PALLADIUM ASSISTED OXIDATION OF CYCLOPENTENE BY MOLECULAR  
OXYGEN

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Dichlorobis(N,N-dialkylacetamide)palladium(II) complex catalyzes the oxidation of cyclopentene to cyclopentanone by molecular oxygen in alcoholic solvent, in which one atom of molecular oxygen is incorporated.

In recent years, intensive efforts have been made to activate molecular oxygen by coordination with a metallic center in order to transfer it to an activated substrate. In the case of olefin oxidation, noble metals are frequently used as the catalyst which can easily activate olefins by coordination. Mimoun et al.<sup>1)</sup> reported that rhodium cationic complexes in alcoholic solvent catalyze the oxidation of terminal olefins to methyl ketones by O<sub>2</sub> activation at room temperature. However, it has not been reported as far as we know by literature surveys that palladium complex catalyzes the oxidation of olefins to ketones by molecular oxygen.

We describe herein a novel oxidation of cyclopentene to cyclopentanone with PdCl<sub>2</sub> complexes by molecular oxygen in alcoholic solvent at room temperature.

Some representative results are shown in Table 1. PdCl<sub>2</sub> complexes of nitriles,<sup>2)</sup> N,N-dimethylacetamide,<sup>3)</sup> and N,N-diethylacetamide<sup>3)</sup> were prepared by the reported methods. PdCl<sub>2</sub> alone slowly catalyzed the ketonization of cyclopentene in anhydrous ethanol. The addition of LiCl slightly enhanced its activity. The use of nitriles as the ligand caused an obvious increase in the activity. The nitrile complexes were, however, not stable and palladium metal deposited during the reaction. The best result was obtained with dichlorobis-(N,N-diethylacetamide)palladium(II) complex [PdCl<sub>2</sub>(DEAc)<sub>2</sub>] (Entry 8). PdCl<sub>2</sub>(DMAc)<sub>2</sub> showed a similar activity (Entry 6). In this case, the O<sub>2</sub> consumption

Table 1. Palladium-assisted oxidation of cyclopentene <sup>a)</sup>

Entry	Pd-complex	Cyclopentanone yield (%)	T.O.F. <sup>b)</sup> (mol/molPd)	Consumed O <sub>2</sub> (mmol)	Reaction time (h)
1	PdCl <sub>2</sub>	3.3	6.4	0.54	8
2	PdCl <sub>2</sub> -LiCl <sup>c)</sup>	5.1	9.8	0.70	8
3	Na <sub>2</sub> PdCl <sub>4</sub>	3.3	6.3	0.60	8
4	PdCl <sub>2</sub> (CH <sub>3</sub> CN) <sub>2</sub>	12.9	24.7	1.42	8
5	PdCl <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> CN) <sub>2</sub>	10.3	19.7	1.22	8
6	PdCl <sub>2</sub> (DMAc) <sub>2</sub>	19.3	37.0	2.49	8
7 <sup>d)</sup>	PdCl <sub>2</sub> (DMAc) <sub>2</sub>	8.6	16.4	0.91	8
8	PdCl <sub>2</sub> (DEAc) <sub>2</sub>	20.1	38.5	2.53	8
9	PdCl <sub>2</sub> (DMAc) <sub>2</sub>	13.7	26.2	1.94	2
10 <sup>e)</sup>	PdCl <sub>2</sub> (DMAc) <sub>2</sub>	13.7	26.2	1.98	2


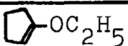
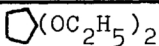
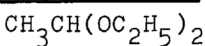
a) A mixture of cyclopentene (1 ml; 11.5 mmol) and palladium complex (0.06 mmol) in anhydrous ethanol (2 ml) was reacted at 30°C under O<sub>2</sub> pressure (860 mmHg). b) Turn over frequency of palladium, c) LiCl, 0.30 mmol, d) *t*-Butyl alcohol was used as solvent. e) 2,6-Di-*t*-butyl-*p*-cresol (0.12 mmol) was added.

occurred immediately after the start of reaction, and the deposition of palladium metal was not observed. The deactivation observed after the reaction time of 2 h ( Entry 6 and 9 ) may be owing to the formation of  $\pi$ -allylic complex as frequently observed in palladium catalyzed oxidation of olefins. The addition of 2,6-di-*t*-butyl-*p*-cresol as a radical inhibitor did not affect the oxidation ( Entry 10 ), showing that no autoxidation is involved.

No catalytic reaction proceeded in benzene, methyl ethyl ketone, dichloromethane, or *N,N*-dimethylacetamide as the solvent. Cyclopentene was catalytically oxidized in ethanol, and *t*-butyl alcohol was less effective ( Entry 7 ). Pd(OCOCH<sub>3</sub>)<sub>2</sub>, Pd(OCOCF<sub>3</sub>)<sub>2</sub>, Pd(acac)<sub>2</sub>, PdSO<sub>4</sub>·2H<sub>2</sub>O, PdO, or Pd black was not active for the oxidation.

The oxidation of cyclopentene with PdCl<sub>2</sub>-*p*-benzoquinone (BQ) couple in ethanol was carried out ( Table 2 ) in order to know the mechanistic character of the palladium catalyzed oxidation cited above. The use of BQ as a reoxidizing agent of Pd(0) to Pd(II) resulted in the Wacker type oxidation,<sup>4)</sup> by which cyclopentanone was formed catalytically via cyclopentenyl ethyl ether. However, PdCl<sub>2</sub> alone showed a quite different product distribution. It is notice-

Table 2. Oxidation of cyclopentene with PdCl<sub>2</sub>-p-benzoquinone<sup>a)</sup>

BQ/Pd (molar ratio)	Products (mmol)				Consumed O <sub>2</sub> (mmol)
					
0	2.32	-	-	0.10	2.33
1	0.90	trace	trace	0.03	0.82
2	0.82	trace	trace	trace	0.65
4	0.97	0.04	0.10	trace	0.78
8	1.15	0.16	0.39	trace	0.56

a) A mixture of cyclopentene (1 ml; 11.5 mmol), PdCl<sub>2</sub> (0.25 mmol), and p-benzoquinone in anhydrous ethanol (2 ml) was reacted at 30°C under O<sub>2</sub> pressure (860 mmHg) for 8 h.

able that PdCl<sub>2</sub> alone gave cyclopentanone with the higher yield and selectivity than the couple and, simultaneously, oxidized ethanol to acetaldehyde and acetal, though the former was not quantitated. When cyclohexene was oxidized, as a comparison, under the same conditions to Table 2, neither cyclohexene nor ethanol was oxidized catalytically with PdCl<sub>2</sub> alone. The PdCl<sub>2</sub>-BQ couple gave catalytically the products of Wacker type oxidation, i.e., cyclohexanone, cyclohexenyl ethyl ether, and cyclohexanone diethyl acetal, the amounts of which increased proportionately with the ratio of BQ/Pd. The formation of acetal, i.e., ethanol oxidation, was also observed remarkably in the oxidation of cyclopentene with PdCl<sub>2</sub>(DEAc)<sub>2</sub> catalyst. The amount of O<sub>2</sub> consumed (mol) nearly corresponds to that of cyclopentanone formed (mol) in the case of using PdCl<sub>2</sub> alone as well as PdCl<sub>2</sub>(DEAc)<sub>2</sub> catalyst. These results suggest that a non Wacker type oxidation of cyclopentene proceeded with the PdCl<sub>2</sub> complex catalyst in ethanol.

Though the details of the reaction cannot be referred clearly in the present work, a possible active species is thought to be palladium hydroperoxide<sup>5)</sup> formed by molecular oxygen insertion into palladium hydride species, of which hydrogen is supplied by ethanol oxidation. Such an active intermediate may be stabilized by the coordination of N,N-DEAc, resulting in the increase in the catalytic activity. This is the first example of the selective oxidation of cyclic olefin to corresponding ketone by molecular oxygen with palladium catalyst. Attempts to increase the catalytic activity of the palladium complex and to establish a

more complete view of the mechanism for the cyclopentene oxidation are under investigation.

#### References

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