Phys. Lett. **117**, 518 (1985).
6. D.W. Boo, W.S. Oh, M.S. Kim, H. Lee and K. Kim, *Chem. Phys. Lett.* **120**, 301 (1985).
7. T.H. Joo, K. Kim and M.S. Kim, *J. Phys. Chem.* **90**, 5816 (1986).
8. T.H. Joo, M.S. Kim and K. Kim, *J. Raman Spectrosc.* **18**, 57 (1987).
9. T.H. Joo, K. Kim and M.S. Kim, *J. Mol. Struct.* **158**, 265 (1987).
10. T.H. Joo, M.S. Kim and K. Kim, *J. Mol. Struct.* in press.
11. J.A. Creighton, C.G. Blatchford and M.G. Albrecht, *J. Chem. Soc. Faraday II*, **75**, 790 (1979).
12. J.H.S. Green and D.J. Harrison, Spectrochim. Acta 32A, 1279 (1976).
13. G. Varsanyi, Ed., Vibrational Spectra of Benzene Derivatives, Academic Press, New York (1969).
14. H. Nichols and R.M. Hexfer, *J. Chem. Phys.* **75**, 3126 (1981).
15. M. Moskovits, *J. Chem. Phys.* **77**, 4408 (1982).
16. M. Moskovits and D.P. Dilella, *J. Chem. Phys.* **73**, 6068 (1980).
17. P. Gao and M.J. Weaver, *J. Phys. Chem.* **89**, 5040 (1985).
18. P. Avouris and J.E. Demuth, *J. Chem. Phys.* **75**, 4783 (1981).
19. B.H. Loo, Y.G. Lee and D.O. Frazier, *Chem. Phys. Lett.* **119**, 312 (1985).
20. C.M. Friend, J. Stein and E.L. Muetterties, *J. Am. Chem. Soc.* **103**, 767 (1981).
21. C.M. Friend, E.L. Muetterties and J. Gland, *J. Phys. Chem.* **85**, 3256 (1981).
22. K. Kishi and S. Ikeda, *Surface Sci.* **107**, 405 (1981).
23. B.A. Sexton and N.R. Avery, *Surface Sci.* **129**, 21 (1983).
24. R.M. Wexler and E.L. Muetterties, *J. Phys. Chem.* **88**, 4037 (1984).
25. M. Moskovits, *J. Chem. Phys.* **75**, 3126 (1981).
26. J.A. Creighton, *Surface Sci.* **124**, 209 (1983).
27. F.R. Dollish, Characteristic Raman Frequencies of Organic Compounds, Wiley, New York (1974).
28. V.M. Hallmark and A. Campion, *J. Chem. Phys.* **84**, 2942 (1986).
29. R.P. Cooney, M.R. Mahoney and M.W. Howard, *Chem. Phys. Lett.* **76**, 448 (1980).
30. C.G. Blatchford, O. Siiman and M. Kerker, *J. Phys. Chem.* **87**, 2503 (1983).

Palladium Dichloro Complex Catalysed Oxidation of Cyclopentene by Dioxygen in Tetralin†

Katsuomi Takehira, Takashi Hayakawa*, Hideo Orita, and Masao Shimizu

National Chemical Laboratory for Industry, Tsukuba Research Center, Yatabe, Ibaraki 305, Japan

In Hwan Oh

Department of Chemistry, Sogang University, Seoul 121. *Received March 19, 1987*

Palladium dichloro complexes catalysed the oxidation of cyclopentene by dioxygen in tetralin solvent at ambient temperature. Cyclopentanone formed mainly together with autoxidation products from both cyclopentene and tetralin. The oxidation seems to proceed by co-oxidation mechanism, where tetralin was first oxidized to its hydroperoxide which then oxidized cyclopentene to cyclopentanone. Mechanism of the other by-products formations has been discussed.

Introduction

Oxygen atom transfer reactions using transition metal complexes and some oxygen donors such as dioxygen, hydrogen peroxide and alkyl hydroperoxides, etc., is one of the current interests and many papers have been published from the following two aspects; the first is concerned with the model reactions for monooxygenase catalysed oxygen atom transfer, and the second is its synthetic utility to produce epoxide or ketone[1]. Concerning to olefin oxidation by noble metal catalysts, it has been reported that a rhodium cationic complex shows catalytic activity for oxygen incorporation from dioxygen,[2] while a palladium peroxo complex can work as the catalyst using *t*-butyl hydroperoxide or hydrogen peroxide as the oxygen doner.[3] In both cases, terminal olefin is the sole substrate which can be readily oxidized to methyl ketone, and the oxidation of internal or cyclic olefin to the corresponding ketone does not proceed so easily under the usual conditions.

We have found that cyclic olefin such as cyclopentene or cyclohexene can be oxidized to the corresponding alicyclic ketone by palladium complex-dioxygen couple in alcoholic solvent[4] or palladium complex-*t*-butyl hydroperoxide couple.[5] In the latter case, *t*-butyl hydroperoxide seems to work as the oxygen donor. We examined here a possibility of the cyclopentene oxidation by dioxygen in tetralin solvent, expecting that α-tetralyl hydroperoxide *in situ* formed can work as the oxygen donor to cyclopentene.

† Dedicated to the 60th birthday of Professor Nung Min Yoon.
* Author to whom correspondence should be addressed.

Table 1. Oxidation of Cyclopentene by Various Metal Complexes in Tetralin

Catalyst	Products(mmol)							O_2-consumed (mmol)
								
$PdCl_2$[a]	0.79	0.45	0.41	0.14	0.06	0.39	1.32	3.92
$PdCl_2(DEAc)_2$[a]	0.35	0.09	0.08	-	-	0.12	0.45	1.03
$PdCl_2(DMAc)_2$[a]	0.25	0.08	0.08	-	-	0.12	0.38	0.76
$PdCl_2(DMF)^{2a}$	0.22	0.10	0.13	-	-	0.22	0.34	0.96
$PdCl_2(DMSO)_2$[a]	0.03	0.01	0.06	-	-	0.18	0.32	0.94
$PdCl_2$[b]	1.04	1.05	1.03	0.16	0.07	1.21	2.23	6.85
$PdCl(acac)_2$[b]	0.42	0.36	0.20	-	-	0.39	0.98	2.90
$RhCl_3.3H_2O$[b]	-	1.26	1.56	0.16	0.04	1.52	2.34	3.72
$RhCl(PPh_3)_3$[b]	-	1.05	1.63	0.10	0.02	2.08	2.42	7.07
$Rh(acac)_3$[b]	-	0.70	0.91	0.11	0.02	2.23	3.20	5.91

Cyclopentene, 1 m*l* (11.4 mmol); Tetralin, 2 m*l*; Catalyst, 0.06 mmol; Reaction temperature, [a]30°C, [b]50°C; Reaction time, 8 h; Oxygen pressure, 860 mmHg.

Experimental Section

Reagents. Oxygen and nitrogen were dried by passage through a single column packed with Linde 3A molecular sieve prior to use. Cyclopentene and tetralin (Aldrich 99%) were commercially available as reagent grade materials. They were passed through a column containing active alumina to remove peroxidic impurities, distilled and stored under nitrogen. Metal complexes were commercially available except mentioned. Palladium dichloro complexes of N,N-dimethylacetamide (DMAc),[6] N,N-diethylacetamide (DMAc),[6] N,N-dimethylformamide (DMF),[6] dimethylsulfoxide (DMSO)[6] and Pd $(OCOCF_3)_2$[7] were prepared by the reported methods.

Oxidation Procedures. The reaction was carried out using a gas sealed system. In a typical procedure, $PdCl_2$ was put into a 10 m*l* double-jacketed glass reactor equipped with a magnetic stirrer, a gas burette and a manometer. After evacuating the reactor with a rotary pump, oxygen gas was introduced and then the reactor was heated at the requested temperature by circulating glycerin-water fluid controlled by thermostat bath. Cyclopentene and tetralin were added and the reaction was then started by vigorous stirring. The evolution of the reaction was followed by oxygen uptake measurements and gas chromatography analysis. The identification of products was done by gas chromatography-mass spectrometry method using Shimadzu GC-MS QP 1000 with authentical samples. A quantitative analysis of products was performed using *o*-dichlorobenzene as an internal standard by Shimadu GC-R1A fitted with a 5 m long column PEG 20M 10% on Uniport B 60/80 at elevated temperature after aliquot sample was treated with sufficient triphenylphosphine for the quantitative conversion of the hydroperoxide to the alcohol.[8] By this treatment, 2-cyclopentenyl-1-hydroperoxide and α-tetralyl hydroperoxide were converted to 2-cyclopenten-1-ol and α-tetralol, respectively. The amount of hydroperoxides could not be determined because metal salts interferred the result of iodometry. Water was quantitated by using a 3 m long column PEG 1000 10% on Flusin T at 130°C.

α-Tetralyl Hydroperoxide Preparation. α-Tetralyl hydroperoxide was prepared by the reported method.[9] Neat tetralin was autoxidized under oxygen atmosphere at 70°C for 48 h, and the reaction mixture was distilled under reduced pressure to recover unoxidized tetralin. The residue containing α-tetralyl hydroperoxide was obtained and its content determined by the iodometric method was 28.5 mol%.

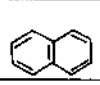
Results and Discussions

Activity of Noble Metal Complexes. Table 1 lists some representative results of the oxidation of cyclopentene with various noble metal complexes in tetralin solvent. Oxygen uptake was observed when using some palladium and rhodium complexes, in which the formers afforded cyclopentanone together with autoxidation products such as 2-cyclopenten-1-one, 2-cyclopenten-1-ol, α-tetralone and α-tetralol. The rhodium complexes catalysed only the autoxidation. The other noble metal complexes such as $PtCl_4.5H_2O$, $H_2PtCl_6.6H_2O$, PtI_2 and $HAuCl_4.4H_2O$ showed no activity. $Pd(OCOCH_3)_2$, $Pd(OCOCF_3)_2$ and $PdSO_4.2H_2O$ caused a rapid deposition of palladium metal, resulting in no oxidation. $PdCl_2(DMSO)_2$ and $PdCl_2(PPh_3)_2$ showed neither oxygen uptake nor oxygenation product; this may be due to their stable coordination structure, It can therefore be reasoned that palladium dichloro complexes possessing the ligand coordinated weakly are generally active for the cyclopentanone production.

Among the palladium dichloro complexes used, $PdCl_2$ revealed the highest activity and the coordination of organic base such as DMAc, DEAc, DMF and DMSO to $PdCl_2$ caused a decrease in the activity. This seems apparently contrast with the result obtained in cyclopentene oxidation to cyclopentanone by palladium complex-dioxygen[4] or -*t*-butyl hydroperoxide[5] couple where the coordination of the base caused an increase in the activity. However, $PdCl_2$ afforded relatively much amount of autoxidation products, while the $PdCl_2$-base complexes showed the more selective formation of cyclopentanone from cyclopentene than $PdCl_2$.

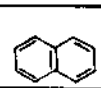
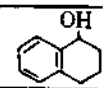
Oxidation Mechanism. $PdCl_2$ caused no oxidation of cyclopentene in benzene or cyclohexane solvent, but oxidized it in tetralin solvent. Neat tetralin was also autoxidized by $PdCl_2$ at 30~50°C. It can therefore be considered that the oxidation of cyclopentene in tetralin solvent proceeds suc-

Table 2. Effect of the Additives in Cyclopentene Oxidation by $PdCl_2$ in Tetralin

Additive (mmol)	Products(mmol)							O_2-consumed (mmol)
								
none	0.67	0.34	0.35	0.03	0.02	0.18	0.75	2.73
AIBN(0.12)	0.58	0.40	0.52	0.12	0.03	0.21	0.70	2.79
$CoCl_2$(0.12)	0.74	0.46	0.42	0.13	0.05	0.38	1.25	3.82
$MnCl_2$(0.12)	0.73	0.49	0.47	0.09	0.05	0.40	1.54	3.88
$CuCl_2$(0.12)	0.03	0.08	0.02	-	-	0.06	0.10	0.29

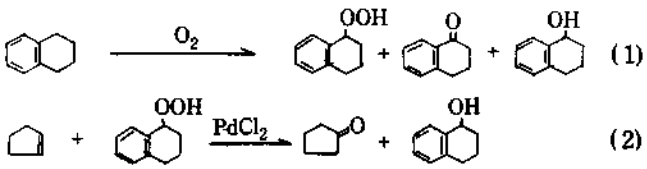
Cyclopentene, 1.5 m*l*(11.4 mmol); Tetralin, 1.5 m*l*; $PdCl_2$, 0.06 mmol; Reaction temperature, 30°C; Reaction time, 8h; Oxygen Pressure, 860 mmHg.

Table 3. Palladium Complex Catalysed Oxidation of Cyclopentene with α-tetralyl Hydroperoxide

Catalyst	Products(mmol)						
							
$PdCl_2$	0.70	0.22	0.19	0.27	0.13	1.64	3.47
$PdCl_2(DEAc)_2$	1.32	0.31	0.22	0.10	0.08	0.85	3.98
$Pd(OCOCH_3)_2$	0.33	0.51	0.13	0.07	0.09	1.35	3.45
$Pd(OCOCF_3)_2$	0.09	0.05	0.16	0.25	0.14	1.14	3.28
$Pd(acac)_2$	0.99	0.22	0.07	0.05	0.16	1.11	3.55
$PdCl_2+CuCl_2$(1/1)	0.46	-	0.07	0.59	0.11	1.32	1.34
$PdCl_2+CuCl_2$(1/2)	0.44	-	0.08	1.07	0.13	1.27	0.89

Cyclopentene, 1 m*l*(11.4 mmol); α-Teralyl hydroperoxide(28.5 mol% solution in tetralin), 2 m*l*(4.0 mmol); palladium complex, 0.25 mmol; Reaction temperature, 50°C; Reaction time, 8h; under nitrogen atmosphere.

cessively *via* the formation of α-tetralyl hydroperoxide as follows:



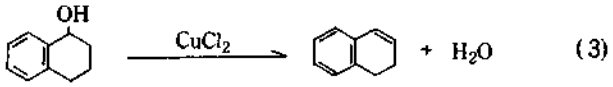
Tetralin is first oxidized to α-tetralyl hydroperoxide, α-tetralone and α-tetralol by the radical chain reaction(1), among which α-teralyl hydroperoxide may work as the oxygen donnor in the presence of palladium complex catalyst by complexing with palladium to form Pd-OOR type active species capable of converting cyclopentene to cyclopentanone(2), as suggested in palladium alkylperoxo complex catalyzed oxidation of terminal olefins.[3] Cyclopentene is simultaneously oxidized by the radical chain reaction and affords 2-cyclopenten-1-one and 2-cyclopenten-1-ol *via* 2-cyclopentenyl-1-hydroperoxide plausibly formed as an intermediate which can also work as the oxygen donnor in reaction(2), though its contribution might be small. The autoxidation of cyclopentene could be initiated by the radical species generated in the tetralin autoxidation, because no oxidation occurred in the tetralin.

The oxidation of cyclopentene with $PdCl_2$ catalyst in tetralin was carried out at 30°C in the presence of additive which might affect the radical chain reaction (Table 2). The addition of α,α'-azobis(isobutyronitrile) (AIBN) as an radical initiator caused a slight shift of the product distribution into the autoxidation type, resulting in a decrease in the amount of cyclopentanone. $CoCl_2$ and $MnCl_2$, both of which can accelerate the radical chain reaction by decomposing homolytically hydroperoxide formed, caused an increase in the amount of the autoxidation products, but susbstantially no increase in that of cyclopentanone. The addition of 2,6-di-*t*-butyl-*p*-cresol as a radical inhibitor resulted in no oxidation, suggesting an importance of the reaction (1). *p*-Benzoquinone as well as $CuCl_2$ can work also as the reoxidizing agent of reduced palladium species, and both the compounds inhibited the oxidation. Therefore, it seems reasonable that the active palladium species is in a lower valency state than Pd(II).

In order to confirm the reaction scheme proposed above, the oxidation of cyclopentene was carried out in the presence of palladium complex and α-tetralyl hydroperoxide under nitrogen atmosphere. α-Tetralyl hydroperoxide used was prepared separately.[9] Typical results are shown in Table 3. Cyclopentanone formation was considerably catalysed by some palladium complexes, among which $PdCl_2(DEAc)_2$ showed the highest activity. The reaction scheme proposed as (1) and (2) seems thus reasonable. The activity of $PdCl_2$ was lowered by the addition of $CuCl_2$ which can reoxidize Pd(0) to Pd(II). This suggests that the active palladium species is not in the Pd(II) state but in the lower valency state as well as observed in Table 2.

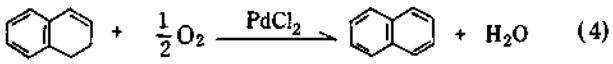
In these reactions, 1,2-dihydronaphthalene and naphthalene were detected as the secondary products, and the $CuCl_2$ addition caused an increase in the amount of the former product. The formations of both the products cannot be explained by the reaction scheme cited above. The fact that an increase in the amount of 1,2-dihydronaphthalene was accompanied with a decrease in that of α-tetralol sug-

gests the following dehydration mechanism:



(3)

$CuCl_2$ or $PdCl_2$, etc., as a Lewis acid catalyst accelerates the dehydration of α-tetralol to 1,2-dihydronaphthalene(3) and the latter is then oxidatively dehydrogenated to naphthalene catalyzed by palladium(II) species(4):



(4)

Each of the reactions(3) and (4) was confirmed by the separate experiments as follows. α-Tetralol afforded 1,2-dihydronaphthalene and water when treated with $CuCl_2$, and 1,2-dihydronaphthalene was catalytically converted to naphthalene by $PdCl_2$ under oxygen atmosphere.

Conclusion

Cyclopentene was catalytically oxidized to cyclopentanone by palladium complex-dioxygen couple in tetralin solvent at ambient temperature. The oxidation proceeded by co-oxidation mechanism, in which tetralin was first oxidized to α-tetralyl hydroperoxide by radical chain reaction and the hydroperoxide as an oxygen donor converted then cyclopentene to cyclopentanone. As the secondary products, 2-cyclopenten-1-one, 2-cyclopenten-1-ol, α-tetralone and α-tetralol formed by the radical chain reaction, and furthermore, 1,2-dihydronaphthalene and naphthalene were produced by the α-tetralol dehydration followed by the oxidative dehydrogenation.

References

1. S. Patai, "The Chemistry of Functional Groups, Peroxide," Wiley-Interscience, New York, 1983.
2. H. Mimoun, M. M. P. Machirant and I. Seree de Roch, *J. Am. Chem. Soc.*, **110**, 5473 (1978).
3. H. Mimoun, R. Charpantier, A. Mitschler, J. Fischer and R. Weiss, *J. Am. Chem. Soc.*, **102** 1048 (1980).
4. K. Takehira, T. Hayakawa and H. Orita, *Chem. Lett.*, 1835 (1985).
5. K. Takehira, unpublished results.
6. B.B. Wayland and R.F. Schramm, *Inorg. Chem.*, 8, 971 (1969).
7. T.A. Stephenson, S.M. Morehouse, A.R. Powell, J.P. Heffer and G. Wilkinson, *J. Chem. Soc.*, 3632 (1965).
8. L. Horner and W. Jurgleit, *Ann. Chem.*, **591** 139 (1955).
9. H.B. Knight and D. Swern, "Organic Synthesis," Col. Vol. IV, p895, John Wilery & Sons, New York (1963).

Asymmetric Reduction of Prochiral α,β-Acetylenic Ketones With Potassium 9-O-(1,2: 5,6-Di-*O*-isopropylidene-α-*D*-glucofuranosyl)-9-boratabicylco[3, 3, 1] nonane†

Byung Tae Cho*

Department of Chemistry, Hallym University, Chuncheon 200

Won Suh Park

Department of Chemisty, Pudue University. U.S.A. *Received March 19, 1987*

The asymmetric reduction of representative prochiral α,β-acetylenic ketones with a new chiral borohydride reducing agent, potassium 9-O-(1,2: 5,6-Di-O-isopropylidene-α-*D*-glucofuranosyl)-9-boratabicyclo[3.3.1]nonane, **1**, in THF at −78°C was studied. Structurally different acetylenic ketones such as internal α,β-acetylenic ketones $RC{\equiv}CCOCH_3$ and terminal α,β-acetylenic ketones $HC{\equiv}CCOR$ were chosen. Thus, the reduction of internal α,β-acetylenic ketones yields the corresponding propargyl alcohols, such as 67% ee for 3-hexyn-2-one, 75% ee for 5-methyl-3-hexyn-2-one, 86% ee for 5,5-dimethyl-3-hexyn-2-one, 74% ee for 3-nonyn-2-one and 61% ee for 4-phenyl-3-butyn-2-one. Terminal α,β-acetylenic ketones, such as 3-butyn-2-one, 1-pentyn-3-one, 4-methyl-1-pentyn-3-one and 1-octyn-3-one, are reduced to the corresponding alcohols with 59% ee, 17% ee, 44% ee and 12% ee of optical induction respectively. With one exception (4-methyl-1-pentyn-3-one), all propargyl alcohols obtained are enriched in R-enantiomers.

Since the acetylenic unit provides a convenient handle for transforming into a variety of functionalities, optically active propargyl alcohols are very useful precursors and intermediates in chiral syntheses of biologically active substances.[1] One of the most convenient methods for the preparation of optically active propargyl alcohols is the asymmetric reduction of α,β-acetylenic ketones with chiral reducing agents.[2]

Recently we discovered a well-difined, new chiral borohydride reducing agent, potassium 9-O-(1,2: 5,6-Di-O-isopropylidene-α-D-glucofuranosyl)-9-boratabicyclo[3.3.1]nonane (K9-O-DIPGF-9-BBNH, K-Glucoride,[3] **1**). This reagent provides highly effective asymmetric induction for a

† Dedicated to Professor Nung Min Yoon on the occasion of his 60th birthday.