RHODIUM(II) ACETATE: AN EFFECTIVE HOMOGENEOUS CATALYST FOR SELECTIVE ALLYLIC OXIDATION AND CARBON-CARBON BOND FISSION OF OLEFINS

Sakae UEMURA[*] and Suresh R. PATIL
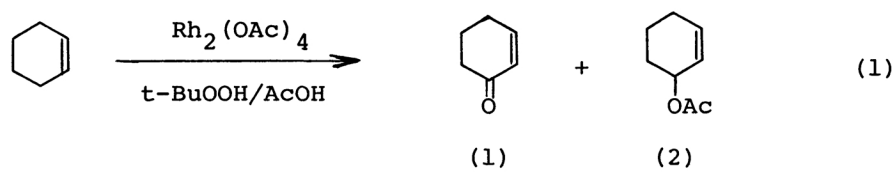
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

Treatment of some cyclic olefins and allylbenzene with $Rh_2(OAc)_4$ in acetic acid in the presence of t-BuOOH gave the corresponding enones and allylic acetates, the former being predominant. Application to several styrene derivatives resulted in a selective C=C bond fission to give benzaldehyde or acetophenone. It is suggested that the reaction proceeds catalytically with Rh(II) acetate via an ionic pathway.

Although the liquid-phase oxidation of olefins is known to be catalyzed by a variety of metal complexes,[1] a few reports have appeared on a catalytic allylic oxidation of olefins. Sharpless et al.[2] and we[3] have reported an effective allylic oxidation of linear and cyclic olefins using SeO_2 and Pd(II) species as catalyst, respectively, the major products being allylic alcohols or acetates. In this letter we wish to report our preliminary results of an investigation on Rh(II) acetate-catalyzed oxidation of olefins where α,β-unsaturated ketones(enones) were obtained as major products from cyclic olefins and allylbenzene in a sharp contrast to the above two reports and, on the other hand, the carbon-carbon double bond fission products were produced from some styrene derivatives.
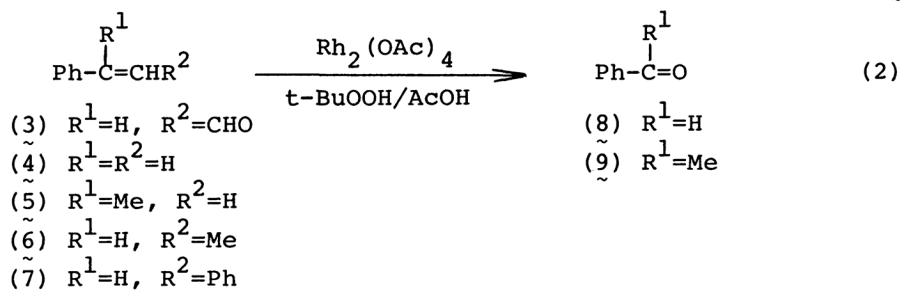
A pale blue homogeneous solution of Rh(II) acetate dimer (0.05 mmol), cyclohexene (10 mmol), 70% t-butyl hydroperoxide (10 mmol) and acetic acid (30 ml) was stirred at 25°C for 3 days. After usual workup procedure (addition of aq. NaCl, extraction with $CHCl_3$, washing with aq. $NaHCO_3$, and drying over Na_2SO_4) GLC analysis revealed the presence of 2-cyclohexen-1-one (1) (2.84 mmol) and 2-cyclohexen-1-yl acetate (2) (0.30 mmol) as products (Eq. 1). No reaction occurred in the absence of either the Rh salt or t-BuOOH under this reaction condition. The oxi-

dation was also observed in the presence of molecular oxygen (1 atm.), hydrogen

peroxide (10 mmol), or m-chloroperbenzoic acid (10 mmol) in the place of t-BuOOH

as re-oxidant, but either the selectivity for (1) or the yield of the products was

low.   Other rhodium compounds such as rhodium(III) chloride ($RhCl_3 \cdot 3H_2O$), tris-

(acetylacetonato)rhodium(III) [$Rh(acac)_3$], and Wilkinson's catalyst [$RhCl(PPh_3)_3$]

were also effective for this oxidation, but either the selectivity or the yield of

the products was lower than those attained by using $Rh_2(OAc)_4$.[4]   It is interesting

that the reactions catalyzed by these latter three compounds in the presence of t-

BuOOH are revealed to be free-radical chain oxidation reactions, since no products

were obtained when 2 mol% (to the starting olefin) of radical scavenger such as

$$\bigcirc \quad \xrightarrow[\text{t-BuOOH/AcOH}]{Rh_2(OAc)_4} \quad \bigcirc\!\!=\!\!O \quad + \quad \bigcirc\!\!-\!\!OAc \qquad (1)$$

$$\underset{\sim}{(1)} \qquad\qquad \underset{\sim}{(2)}$$

6-t-butyl-o-cresol or hydroquinone was added.   In contrast to this, the oxidation

reactions using Rh(II) acetate were affected only a little by those scavengers,

the facts suggesting an ionic nature of the reaction.[5]   On the other hand, when

molecular oxygen was used as re-oxidant, even Rh(II) acetate-catalyzed reaction

was found to be free-radical in nature as in the case of the reported $RhCl(PPh_3)_3/$

O_2 system.[6]   The reaction can be applied well to cyclopentene, cycloheptene and

allylbenzene to give mainly the corresponding enones together with some allylic

acetates.[7]   Typical results are shown in Table 1.

In the case of allylbenzene a formation of benzaldehyde was also observed and

this might be formed from a primary product, cinnamaldehyde ($\underset{\sim}{3}$), under these re-

action conditions.   We have separately confirmed that this is actually the case.

Thus, application of the reaction to some styrene derivatives such as ($\underset{\sim}{3}$)-($\underset{\sim}{7}$)

$$\underset{Ph-C=CHR^2}{\overset{R^1}{\,\,|\,\,}} \quad \xrightarrow[\text{t-BuOOH/AcOH}]{Rh_2(OAc)_4} \quad \underset{Ph-C=O}{\overset{R^1}{\,\,|\,\,}} \qquad (2)$$

(3) R^1=H, R^2=CHO   (8) R^1=H
$\underset{\sim}{}$
(4) R^1=R^2=H   (9) R^1=Me
$\underset{\sim}{}$
(5) R^1=Me, R^2=H
$\underset{\sim}{}$
(6) R^1=H, R^2=Me
$\underset{\sim}{}$
(7) R^1=H, R^2=Ph
$\underset{\sim}{}$

resulted in a selective formation of the carbon-carbon double bond fission products

such as benzaldehyde ($\underset{\sim}{8}$) and acetophenone ($\underset{\sim}{9}$) together with small amounts of un-

Table 1.   Rh(II) acetate-catalyzed allylic oxidation of olefins.[a]

Olefin (mmol)	Oxidant[b] (10 mmol)	Products[c] (mmol)		Ratio enone/allylic compd.
Cyclopentene 10	t-BuOOH	(cyclopentenone) 2.32	(cyclopentenyl-OAc) 0.06	38.7
Cyclohexene 10	t-BuOOH	(1) 2.84	(2) 0.30	9.5
Cyclohexene 20	t-BuOOH	(1) 4.69	(2) 1.01	4.6
Cyclohexene[d] 20	t-BuOOH	(1) 3.60	(2) 0.81	4.4
Cyclohexene[e] 20	t-BuOOH	(1) 3.90	(2) 0.96	4.1
Cyclohexene 20	O_2	(1) 1.70	(2) 0.63	2.7
Cyclohexene[e] 20	O_2	(1) 0	(2) 0	
Cyclohexene 20	H_2O_2	(1) 2.45	(2) 0.78[f]	3.1
Cyclohexene 20	MCPBA	(1) 0.96	(2) 0.29[g]	3.3
Cycloheptene 10	t-BuOOH	(cycloheptenone) 1.92	(cycloheptenyl-OAc) 0.10	19.2
Allylbenzene 10	t-BuOOH	(8) 1.33 (3) 0.79 $PhCH=CHCH_2OH$ 0.36[h]		

[a] $Rh_2(OAc)_4$ (0.05 mmol) and AcOH (30 ml) were used.   At 25°C for 3 days.   [b] 70% t-BuOOH; 30% H_2O_2; O_2 (1 atm.); MCPBA = m-chloroperbenzoic acid.   [c] Determined by GLC.   [d] 6-t-Butyl-o-cresol (2 mol% to olefin) was added.   [e] Hydroquinone (2 mol%) was added.   [f] Cyclohexanediol monoacetate (not estimated) is among the products.   [g] Cyclohexanediol monoacetate (4.73 mmol) was the main product.   [h] Allylbenzene (2.30 mmol) was recovered.

Table 2.   Rh(II) acetate-catalyzed C=C bond fission of styrene derivatives.[a]

Olefin (mmol)		Products (mmol)[b]			Recovered olefin (mmol)[b]
(3)	10	(8) 4.08			5.28
(3)[c]	10	(8) 1.15			6.58
(4)	10	(8) 2.73	(9)	0.11	0
(4)	20	(8) 4.36	(9)	0.28	-[d]
(4)[c]	20	(8) 0.80	(9)	trace	-[d]
(4)[e]	20	(8) 3.66	(9)	0.23	-[d]
(5)	10	(9) 8.41			0[f]
(6)	20	(8) 3.90[f]			-[d]
(7)	10	(8) 2.52			-[d]

[a] $Rh_2(OAc)_4$ (0.05 mmol), t-BuOOH (10 mmol) and AcOH (30 ml) were used.   At 25°C for 3 days.   [b] Determined by GLC.   [c] Without $Rh_2(OAc)_4$.   [d] Not determined.   [e] 6-t-Butyl-o-cresol (2 mol% to olefin) was added.   [f] Some high-boiling products were also formed.

identified compounds (Eq. 2; Table 2).[8]   Although such bond fission has been known to occur with some of these olefins by using $RhCl(PPh_3)_3$, $RhCl_3$, or $[RhCl-(C_2H_4)_2]_2$ as catalyst in the presence of oxygen, the reactions have been carried out at higher temperature, the selectivity for (8) or (9) and the turnover number being sometimes not so high.[9]

In the oxidation of cyclic olefins the reaction may proceed via t-butylperoxy-, acetoxy-, and/or hydroxyrhodation followed by dehydrorhodation (β-hydride elimination) as proposed in the cases of allylic oxidation of olefins by Pd(II) acetate,[10] but the details are not yet clear at the present stage.

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

2) M. A. Umbreit and K. B. Sharpless, J. Am. Chem. Soc., 99, 5526(1977).

3) S. Uemura, S. Fukuzawa, A. Toshimitsu, and M. Okano, Tetrahedron Lett., 23, 87(1982).

4) Recently we found a special Rh(III) compound, $[Rh_3O(OAc)_6(H_2O)_3]OAc$, to be effective for a selective formation of enones from some cyclic olefins: S. Uemura and S. R. Patil, Tetrahedron Lett., in press.

5) Similar trend was also observed in the oxidation of styrene which gives benzaldehyde (See Table 2).

6) V. P. Kurkov, J. Z. Pasky, and J. B. Lavigne, J. Am. Chem. Soc., 90, 4743(1968).

7) Although cinnamyl acetate was not obtained from allylbenzene, the oxidation of estragole(p-methoxyallylbenzene) (20 mmol) afforded p-methoxycinnamyl acetate (1.24 mmol) and the corresponding alcohol (0.26 mmol) under similar reaction conditions.   In the case of cycloolefins the formation of small amounts of allylic alcohols was also observed, and those were determined as acetates after acetylation with Ac_2O/pyridine.

8) This C=C bond fission occurs even without Rh(II) acetate, but the yield of the product is very low, the facts showing clearly that Rh(II) acetate catalyzes this oxidation as well (See Table 2).   The formation of acetaldehyde was confirmed as 2,4-dinitrophenylhydrazone derivative(mp 146°C) in the oxidation of (6), although its amount has not been estimated exactly.

9) K. Takao, M. Wayaku, Y. Fujiwara, T. Imanaka, and S. Teranishi, Bull. Chem. Soc. Jpn., 43, 3898(1970); J. Farrar, D. Holland, and D. J. Miller, J. C. S. Dalton, 1975, 815.

10) See for example, W. Kitching, Z. Rappoport, S. Winstein, and W. G. Young, J. Am. Chem. Soc., 88, 2054(1966); S. Wolfe and P. G. C. Campbell, ibid., 93, 1497(1971).