

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

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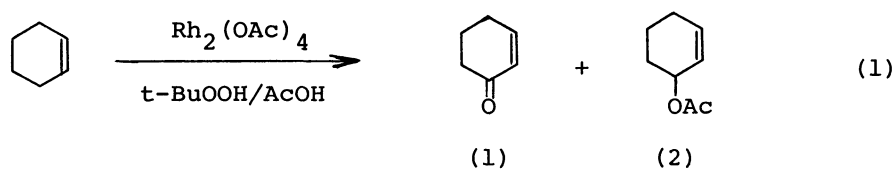
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Treatment of some cyclic olefins and allylbenzene with $\text{Rh}_2(\text{OAc})_4$ in acetic acid in the presence of *t*-BuOOH gave the corresponding enones and allylic acetates, the former being predominant. Application to several styrene derivatives 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 we³⁾ 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.

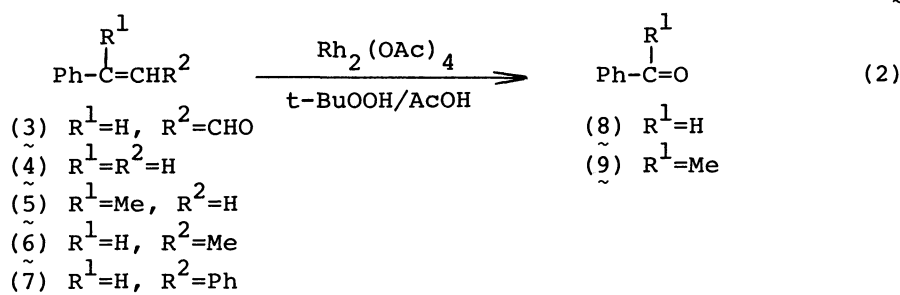
A pale blue homogeneous solution of Rh(II) acetate dimer (0.05 mmol), cyclohexene (10 mmol), 70% *t*-butyl hydroperoxide (10 mmol) and acetic acid (30 ml) was stirred at 25°C for 3 days. After usual workup procedure (addition of aq. NaCl, extraction with CHCl_3 , washing with aq. NaHCO_3 , and drying 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 ($\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$), tris-(acetylacetonato)rhodium(III) [$\text{Rh}(\text{acac})_3$], and Wilkinson's catalyst [$\text{RhCl}(\text{PPh}_3)_3$] were also effective for this oxidation, but either the selectivity or the yield of the products was lower than those attained by using $\text{Rh}_2(\text{OAc})_4$.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







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 $\text{RhCl}(\text{PPh}_3)_3/\text{O}_2$ 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 (3), under these reaction conditions. We have separately confirmed that this is actually the case. Thus, application of the reaction to some styrene derivatives such as (3)-(7)



resulted in a selective formation of the carbon-carbon double bond fission products such as benzaldehyde (8) and acetophenone (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		2.32	 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 ₂ O 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		1.92	 0.10	19.2
Allylbenzene	10 t-BuOOH	(8)	1.33	(3) 0.79 PhCH=CHCH ₂ OH 0.36 ^h	

^aRh₂(OAc)₄ (0.05 mmol) and AcOH (30 ml) were used. At 25°C for 3 days. ^b70% t-BuOOH; 30% H₂O₂; O₂ (1 atm.); MCPBA = m-chloroperbenzoic acid. ^cDetermined by GLC. ^d6-t-Butyl-o-cresol (2 mol% to olefin) was added. ^eHydroquinone (2 mol%) was added. ^fCyclohexanediol monoacetate (not estimated) is among the products. ^gCyclohexanediol monoacetate (4.73 mmol) was the main product. ^hAllylbenzene (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

^aRh₂(OAc)₄ (0.05 mmol), t-BuOOH (10 mmol) and AcOH (30 ml) were used. At 25°C for 3 days. ^bDetermined by GLC. ^cWithout Rh₂(OAc)₄. ^dNot determined. ^e6-t-Butyl-o-cresol (2 mol% to olefin) was added. ^fSome 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 $\text{RhCl}(\text{PPh}_3)_3$, RhCl_3 , or $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ 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.

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- 4) Recently we found a special Rh(III) compound, $[\text{Rh}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]\text{OAc}$, 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.
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