

[Rh₃O(OAc)₆(H₂O)₃]OAc AS A HOMOGENEOUS CATALYST FOR SELECTIVE
ENONE FORMATION BY ALLYLIC OXIDATION OF OLEFINS

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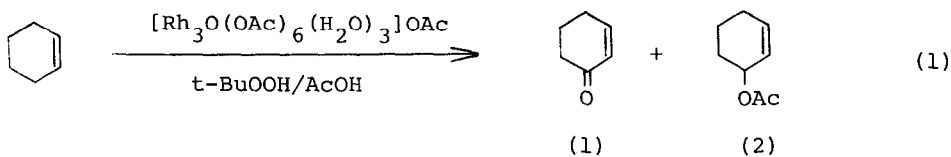
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Summary: Treatment of several cyclic olefins and allylbenzene with a catalytic amount of [Rh₃O(OAc)₆(H₂O)₃]OAc in acetic acid in the presence of t-butyl hydroperoxide affords the corresponding α,β -unsaturated carbonyl compounds (enones) highly selectively via an ionic pathway.

μ_3 -Oxotrimetal acetato-complex of rhodium, [Rh₃O(OAc)₆(H₂O)₃]OAc, prepared by the interaction of hydrated rhodium(III) chloride and silver acetate¹ or by ozonolysis of rhodium(II) acetate² in acetic acid has scarcely been used as catalyst for organic syntheses³ in a contrast to many useful rhodium catalysts. We report here a first clear-cut example for the catalytic activity of this "Rh₃O" complex which works as an effective catalyst for the homogeneous allylic oxidation of olefins in acetic acid to give α,β -unsaturated carbonyl compounds (enones) in the presence of t-butyl hydroperoxide as an oxidizing agent. The result is in a sharp contrast to the recently reported palladium-catalyzed allylic oxidation of olefins under similar conditions where the allylic acetates are obtained highly selectively.⁴

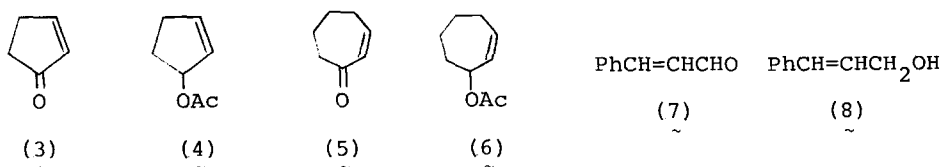
A pale yellow homogeneous solution of cyclohexene (20 mmol), "Rh₃O" complex (0.033 mmol), 70% t-BuOOH (10 mmol), and acetic acid (30 ml) was stirred at 25°C for 3 days. After usual workup procedure (addition of aq. NaCl, extraction with CHCl₃, washing with aq. NaHCO₃, drying over Na₂SO₄) GLC analysis of the extract revealed the presence of 2-cyclohexenone (1) (5.22 mmol) and 2-cyclohexenyl acetate (2) (1.03 mmol) as products (eq. 1). Without the rhodium complex or t-BuOOH the reaction hardly occurred. Similar reaction also took place by

using rhodium(III) chloride hydrate [$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$], rhodium acetylacetonate [$\text{Rh}(\text{acac})_3$], and Wilkinson's catalyst [$(\text{Ph}_3\text{P})_3\text{RhCl}$] in place of " Rh_3O " complex, but either the selectivity for (1) or the yield of the product was lower. The



reactions catalyzed by these latter three catalysts were revealed to be free radical-chain oxidations as in the case of the reported autoxidation of cyclohexene and ethylbenzene,⁵ since no products were obtained when 2 mol% of radical scavengers such as hydroquinone and 6-t-butyl-o-cresol were added. On the contrary, the oxidation reactions using " Rh_3O " complex are not affected so much by the addition of those radical scavengers, the facts suggesting an ionic nature of the reactions. The results are also in contrast to the recently reported $(\text{Ph}_3\text{P})_3\text{RhCl}$ -catalyzed oxidation of anthracene, tetramethylethylene, and trans- and cis-stilbene with oxygen and t-BuOOH where the reaction has been revealed to have a radical nature.⁶

This " Rh_3O " complex-catalyzed oxidation reaction can be applied well to cyclopentene, cycloheptene, and allylbenzene to give mainly the corresponding α,β -unsaturated carbonyl compounds [(3), (5), (7)] together with some allylic acetates or alcohols [(4), (6), (8)].⁷ Typical results are shown in Table 1. All results are reproducible.



In connection with the reaction scheme the following experimental results should be noted: i) cyclohexene oxide is not the precursor of (1) and (2). ii) (2) can not be oxidized to (1), while 2-cyclohexenol and (8) are oxidized

to (1) and (7), respectively, under the reaction conditions.⁸ iii) The oxidation of cyclohexene hardly occurs by use of the stoichiometric amount of " Rh_3O " complex in the absence of t-BuOOH. iv) In UV-visible spectrum, the absorption maximum and its intensity of the complex in acetic acid (λ_{max} 370 nm, $\epsilon=1800$) show no change by addition of t-BuOOH at 25°C even after 48 h, but in the presence of cyclohexene a new absorption due to 2-cyclohexenone appears gradually at λ_{max} 330 nm and covers up the absorption due to the complex. Although it is not yet clear whether the complex maintains its oxo-centred or cyclic structure or is broken down to monomeric Rh(III) species containing t-BuOO moiety as ligand anion, one of the possible reaction schemes is the acetoxo- and/or hydroxyrhodation of olefins, just like as well-known oxymetallation, followed by dehydrorhodation

Table 1. Rh-catalyzed allylic oxidation of olefins in acetic acid.^a

Olefin	Catalyst ^b	Products (mmol)		the ratio of enone/allylic acetate or alcohol
Cyclopentene	" Rh_3O "	(3) 3.08	(4) 0.45	6.8
Cyclohexene	" Rh_3O "	(1) 5.22	(2) 1.03	5.1
Cyclohexene	" Rh_3O " ^c	(1) 6.03	(2) 1.03	5.9
Cyclohexene	" Rh_3O " ^d	(1) 4.29	(2) 0.56	7.7
Cyclohexene	" Rh_3O " ^e	(1) 3.91	(2) 1.08	3.6
Cyclohexene	$\text{Rh}(\text{acac})_3$ ^f	(1) 2.64	(2) 1.44	1.8
Cyclohexene	$\text{RhCl}(\text{Ph}_3\text{P})_3$ ^f	(1) 3.68	(2) 0.99	3.7
Cyclohexene	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ^f	(1) 3.35	(2) 1.15	2.9
Cycloheptene	" Rh_3O "	(5) 2.86	(6) 0.48	6.0
Allylbenzene	" Rh_3O "	(7) 2.31	(8) 0.41	5.6

^aAcOH(30 ml) and olefin(20 mmol) were used. At 25°C for 72 h.

^b" Rh_3O "= $[\text{Rh}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]\text{OAc}$, 0.033 mmol; other catalysts, 0.1 mmol.

^cFor 120 h. ^d6-t-Butyl-o-cresol(2 mol%) was added. ^eHydroquinone

(2 mol%) was added. ^fIn the presence of 2 mol% of 6-t-butyl-o-cresol or hydroquinone, no products were obtained.

to afford allylic acetates and/or alcohols. The produced Rh-hydride complex may be re-oxidized by *t*-BuOOH to active Rh(III) species, the allylic alcohol formed being oxidized further to α,β -unsaturated carbonyl compounds as shown above.

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References and Notes

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7. In the case of cyclic olefins the formation of some allylic alcohols was also observed, and those were determined as (2), (4), and (6) after acetylation with Ac_2O /pyridine.
8. From 2-cyclohexenol(5 mmol), 1.24 mmol of (1) was obtained by stirring at 25°C for 3 days, 1.25 mmol of the starting alcohol being recovered unreacted. Similarly, 0.47 mmol of (7) was formed from (8) (2.5 mmol) at 25°C for 1 day, 0.70 mmol of (8) being recovered.

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