



# Highly selective oxidation of unsaturated hydrocarbons to carbonyl compounds by two-phase catalysis



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## ABSTRACT

An efficient method for selective oxidation of unsaturated hydrocarbons to carbonyl compounds was established by using oxidant [bis(acetoxy)iodo]benzene and catalyst ruthenium trichloride (0.1 mol %) in a  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  two phase system at 30 °C. Both aromatic and aliphatic olefins could be oxidized via direct carbon–carbon bond cleavage to the corresponding aryl or alkyl aldehydes with good selectivity (up to 100%). Further, diketone could be obtained from alkyne in high yields with this method.

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## 1. Introduction

The oxidation of unsaturated hydrocarbon is a significant reaction in organic chemistry, petrochemical industry as well as conversion of biomass. The aldehyde and ketone are important precursors to acid and alcohol as well as widely used in medicine, agriculture, and fine chemical industry.<sup>1–3</sup> Up to now, the selective transformation of unsaturated hydrocarbon to aldehyde or ketone is still a challenging objective, since the result in most cases is workup conditions dependent.<sup>4,5</sup> The most common method for the direct oxidative cleavage of olefins was ozonolysis,<sup>6</sup> but ozone gas is highly toxic and its generation requires specialized equipment.<sup>7</sup> Other oxidants such as  $\text{KMnO}_4$ ,<sup>8</sup> oxone,<sup>9,10</sup>  $\text{NaIO}_4$ ,<sup>11</sup> *m*-CPBA,<sup>12,13</sup> and *t*-BuOOH<sup>14,15</sup> were used to this kind of oxidation reaction. However, the problems of long reaction period, low selectivity, and environment unfriendly are still not resolved. In order to improve the selectivity of products, here we used a two-phase  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  system for the oxidation reaction of olefin and alkyne to achieve aldehyde or diketone products through using  $\text{PhI}(\text{OAc})_2$  as an oxidant and  $\text{RuCl}_3$  as catalyst. The new method is very effective for the selective oxidation of unsaturated hydrocarbons to carbonyl compounds, and the catalyst can be separated easily.

## 2. Experimental

### 2.1. Materials

Ruthenium(III) trichloride, dichloromethane, [bis(acetoxy)iodo]benzene, sodium periodate, 30% hydrogen peroxide, 1-(3,4-dimethoxyphenyl)ethanone, acetonitrile, ethyl acetate, benzene, acetone, and the substrates of olefins and alkynes were analytical grade and purchased from commercial sources and used with certain purification. The concentration of hydrogen peroxide was examined by titrating a standardized ceric sulfate solution to pale blue endpoint with a ferroin indicator.

### 2.2. Methods and instrumentations

The typical solution containing 1 mmol of substrates, 0.1 mol %  $\text{RuCl}_3$ , and 3 equiv of  $\text{PhI}(\text{OAc})_2$ , was heated and kept at constant 30 °C. Reaction products were separated and analyzed by GC–MS (Agilent 5973 Network 6890N, Japan) and NMR (Bruker DPX-300FX). The concentrations of reactant and product in the reaction solution were quantitatively analyzed by Gas chromatography (FULI9790, China). NMR data were recorded using  $\text{CDCl}_3$  as solvent with TMS as an internal standard. Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). GC data was obtained FID gas chromatograph system equipped with a KB-5 capillary column using *p*-nitrotoluene as an internal standard. Electrospray mass spectrometry (ESI-MS) measurements were performed with a TSQ quantum ultra.

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### 2.3. Synthesis of 1-methoxy-4-vinylbenzene

1-Methoxy-4-vinylbenzene was prepared according to literatures.<sup>16–18</sup> It was characterized by ESI-MS:  $m/z$  135.08 (Calcd for  $[M^++1]$ : 135.07);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.85 (s, 3H), 5.16–5.19 (dd,  $J=10.8$  8.0 Hz, 1H), 5.64–5.68 (dd,  $J=17.6$  8.0 Hz, 1H), 6.67–6.75 (m, 1H), 6.90–6.92 (m, 2H), 7.38–7.41 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.36, 136.23, 130.42, 127.41, 113.91, 111.60, 55.31. The NMR spectra in the ESI.

## 3. Results and discussion

### 3.1. Effect of solvent

Solvent displayed important influence on many oxidation reactions.<sup>19–21</sup> To investigate the solvent effect, styrene, *trans*-stilbene, 1-octene, and 1,2-diphenylethyne were chosen as substrates to carry out oxidation reaction by using oxidant  $\text{PhI}(\text{OAc})_2$  and catalyst  $\text{RuCl}_3$  in four kinds of two-phase systems dichloromethane/water, acetonitrile/water, acetone/water, and benzene/water, respectively. The experimental results were listed in Table 1. It can be seen that the oxidation of these substrates afforded small amount of products when acetonitrile/water, acetone/water, and benzene/water were used as solvent systems. Dichloromethane/water was the best solvent system to afford desired product aldehyde or diketone with good yield in relatively short time. It can be further found that the volume ratio of  $\text{CH}_2\text{Cl}_2$  to  $\text{H}_2\text{O}$  had great influence on the oxidation reaction of styrene (Table S1 in the ESI). From Table S1, it can be observed that the two-phase system of 4:1 ratio of  $\text{CH}_2\text{Cl}_2$  to  $\text{H}_2\text{O}$  gave the best results of 100% conversion of styrene and 99.8% yield of benzaldehyde.

### 3.2. Effect of oxidant

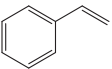
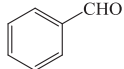
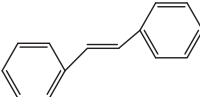
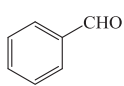
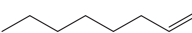
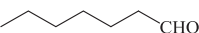
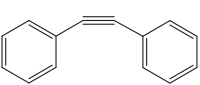
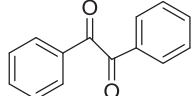
The chemistry of polyvalent iodine compounds has experienced an unprecedented, explosive development during the past few decades. This increasing interest is mainly due to the very useful oxidizing properties of polyvalent iodine reagents combined with their benign environmental nature and commercial availability.<sup>22,23</sup>  $\text{PhI}(\text{OAc})_2$  was used as an oxidant for the oxidation of alcohols,<sup>24,25</sup> phenol,<sup>26,27</sup> and olefin aziridination

reaction.<sup>28</sup> Although some studies on oxidation of olefins to aldehydes or ketones with  $\text{PhI}(\text{OAc})_2$  have been reported in the past few years,<sup>22,29</sup> the disadvantages of slow reaction rate, additional oxidants, and low selectivity still exist. In this work, five oxidants were employed to carry out the oxidation reaction. As seen in Table 2, the substrates styrene, *trans*-stilbene, and 1,2-diphenylethyne can't be oxidized by oxidants  $\text{H}_2\text{O}_2$  and  $\text{Fe}_2(\text{SO}_4)_3$  under the same conditions. However the oxidants *m*-CPBA,  $\text{NaIO}_4$ , and  $\text{PhI}(\text{OAc})_2$  were efficient, and best results could be achieved with  $\text{PhI}(\text{OAc})_2$  as oxidant.  $\text{RuCl}_3$  is one of the commonly used reagent for the oxidation reactions of olefins to aldehydes.<sup>19,30,31</sup> To examine the catalytic activity of catalyst, oxidation cleavage of styrene by  $\text{PhI}(\text{OAc})_2$  catalyzed by various metal salts was comparatively investigated (Table S2 in the ESI). As seen in Table S2, for  $\text{RuCl}_3$  catalyzed system, the reaction was satisfactory that the conversion of styrene achieved 100% after 1.5 h, and the yield of benzaldehyde achieved 99.8% at a low catalyst load of 0.1 mol %. It can be observed that other metal halides showed low catalytic activity for both conversion of styrene and yield of benzaldehyde. It should be noted that only 12.7% conversion of styrene and 10.8% yield of benzaldehyde could be obtained after 4 h in the absence of catalyst.

### 3.3. Oxidative cleavage of terminal olefins

Under the optimum conditions, various aryl- and alkyl-substituted terminal olefins were investigated and the experimental results were listed in Table 3. As observed from Table 3, the  $\text{RuCl}_3$ – $\text{PhI}(\text{OAc})_2$ – $\text{CH}_2\text{Cl}_2$ – $\text{H}_2\text{O}$  system showed excellent catalytic ability for the oxidative cleavage of terminal olefins to aldehydes. The aromatic terminal olefins with electron-rich and electron-poor substituted group in the para position (2a–6a) were oxidized to the corresponding aldehydes in high yields (76.2–92.1%, Table 3, entries 2–6). Styrene (1a) and 2-vinylnaphthalene (7a) were converted to benzaldehyde and 2-vinylnaphthaldehyde in 99.8% and 57.5% yields, respectively (Table 3, entries 1 and 7). The GC profiles of styrene oxidation reaction solution were shown in Figs. 1S–2S. However, when aliphatic alkene was employed, this catalysis reaction showed slow reaction rate. For the oxidation of 1-octene (8a), although the selectivity of the product heptanal (8b) was high (97.5%), only 22.6% yield was obtained after 1.5 h reaction.

**Table 1**  
The yields of carbonyl compounds for the oxidation of unsaturated hydrocarbon in various solvent systems<sup>a</sup>

Substrate	Product	Time (h)	Yield (%)			
			Dichloro-methane <sup>b</sup>	Acetonitrile	Acetone	Benzene
		1.5	99.8	14.5	56.0	52.5
		1.5	99.7	21.4	58.1	31.6
		1.5	22.6	—	7.3	3.2
		2.0	89.6	24.6	63.0	32.5

<sup>a</sup> The reactions were carried out by using oxidant  $\text{PhI}(\text{OAc})_2$  and catalyst  $\text{RuCl}_3$  in 5 mL solvent (organic solvent: $\text{H}_2\text{O}$ =4:1, v/v), GC yields are given. — represent for no reaction.

<sup>b</sup> Isolated yields are given, see ESI for details.

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