

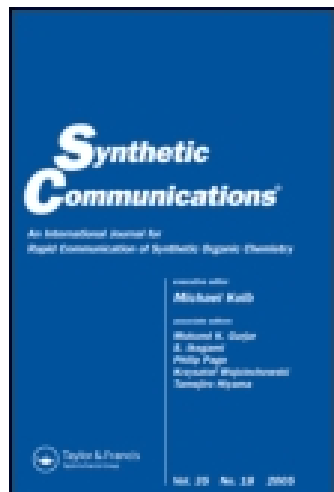
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## Improved Procedure for Ruthenium-Catalyzed Oxidative Cleavage of Alkenes With $\text{IO}(\text{OH})_5$

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**Abstract:** Oxidative cleavage of alkenes to carboxylic acids catalyzed by *cis*- $[\text{RuCl}_2(\text{bipy})_2] \cdot 2\text{H}_2\text{O}$  in the presence of  $\text{IO}(\text{OH})_5$  has been studied in a biphasic ( $\text{CH}_3\text{CN}-\text{CCl}_4-\text{H}_2\text{O}$ ; 1 : 1 : 2 v/v) solvent system. Ruthenium tetraoxide seems to be the active catalyst species.

**Keywords:** Alkenes, cleavage, oxoruthenates

### INTRODUCTION

There are a number of systems in which  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  has been used as a catalyst for oxidative cleavage of alkenes to acids.<sup>[1–3]</sup> Wolfe et al.<sup>[1]</sup> reported the oxidation of cyclohexene to adipic acid by stirring a solution of cyclohexene in  $\text{CH}_2\text{Cl}_2$  with an aqueous solution of  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  and  $\text{NaOCl}$ . The most widely used procedure is that reported by Carlesen et al.,<sup>[2]</sup> in which cyclopentene was converted into glutaric acid by using  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  as catalyst with  $\text{NaIO}_4$  as a cooxidant in a biphasic  $\text{CH}_3\text{CN}-\text{CCl}_4-\text{H}_2\text{O}$  solution. Halostyrenes and haloalkenes were oxidized to their acids using  $\text{RuO}_2 \cdot n\text{H}_2\text{O}$  with either  $\text{NaIO}_4$  or  $\text{NaOCl}$  as cooxidants.<sup>[3]</sup> However, a disadvantage of these catalyst systems is the formation of  $\text{NaIO}_3$  and/or  $\text{NaCl}$  during the oxidation reaction, and they are sparingly

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soluble in water with the solvent quantity specified ( $5\text{ cm}^3$ ).<sup>[2,3]</sup> These solids remain at the end of the reaction, making the workup difficult.

The complex  $cis\text{-}[\text{RuCl}_2(\text{bipy})_2] \cdot 2\text{H}_2\text{O}$  was used for the chemoselective degradation of aromatic rings to acids with  $\text{NaIO}_4$  as a cooxidant<sup>[4]</sup> but not for the oxidative cleavage of alkenes to acids. As a part of our continuing study on the use of ruthenium catalysts for specific oxidation of organic compounds,<sup>[5,6]</sup> we studied the use of the catalyst system  $cis\text{-}[\text{RuCl}_2(\text{bipy})_2] \cdot 2\text{H}_2\text{O}/\text{IO}(\text{OH})_5$  for the oxidative cleavage of alkenes to acids with  $\text{IO}(\text{OH})_5$  as cooxidant; in this system, the direct use of  $\text{RuO}_4$  is avoided.





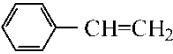
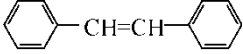



## RESULTS AND DISCUSSION

Although the complex  $cis\text{-}[\text{RuCl}_2(\text{bipy})_2] \cdot 2\text{H}_2\text{O}$  has occasionally been used for other oxidations, few experimental details are available.<sup>[4]</sup> We studied the reaction of  $cis\text{-}[\text{RuCl}_2(\text{bipy})_2] \cdot 2\text{H}_2\text{O}$  with  $\text{IO}(\text{OH})_5$  in a biphasic solvent system for cleavage of alkenes to acids. After many trials, we found that the catalyst system,  $cis\text{-}[\text{RuCl}_2(\text{bipy})_2] \cdot 2\text{H}_2\text{O}/\text{IO}(\text{OH})_5$ , is a highly effective catalyst for oxidative cleavage of a number of linear and cyclic alkenes at room temperature in a biphasic solvent ( $\text{CH}_3\text{CN}-\text{CCl}_4\text{-H}_2\text{O}$ ). In a typical experiment, an aqueous solution of an excess amount of  $\text{IO}(\text{OH})_5$  was added to a stirred solution of an alkene and a catalytic amount of  $cis\text{-}[\text{RuCl}_2(\text{bipy})_2] \cdot 2\text{H}_2\text{O}$  in  $\text{CCl}_4\text{-CH}_3\text{CN}$ , where after stirring for 15 min the brown color of the reaction mixture turned into pale yellow, which is due to the formation of  $\text{RuO}_4$ .

The results obtained for the oxidation of several alkenes by the present catalyst system are summarized in Table 1. We found that the yields of the acids are in the range of 70–92%. These results are comparable to those previously reported by us for the use of the  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}/\text{IO}(\text{OH})_5$  catalyst system for oxidative cleavage of alkenes to acids,<sup>[6]</sup> and the yields here are higher than those previously reported for other catalyst system,  $[\text{RuCl}_2(\text{PPh}_3)_3]/\text{PhIO}$ .<sup>[7]</sup> It was found that the procedure is simple and easy to use, and the major product here is the corresponding acid. Other products such as epoxides were detected but in a very low yields (5%).

The attempts to use other cooxidants, such as  $\text{NaIO}_4$  and  $\text{NaOCl}$ , with  $cis\text{-}[\text{RuCl}_2(\text{bipy})_2] \cdot 2\text{H}_2\text{O}$  under the same conditions for oxidative cleavage of cyclohexene as representative example were all unsuccessful. We noticed that the presence of acetonitrile in the solvent system improves the yields of acids as has been observed for  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}/\text{IO}(\text{OH})_5$  and  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}/\text{NaIO}_4$  systems respectively.<sup>[2,6]</sup> Large-scale oxidation of alkenes to acids can be attained by this catalyst system; for example, oxidation of 20 mmol of styrene gave 19 mmol of benzoic acid with the catalytic turnover of 190.

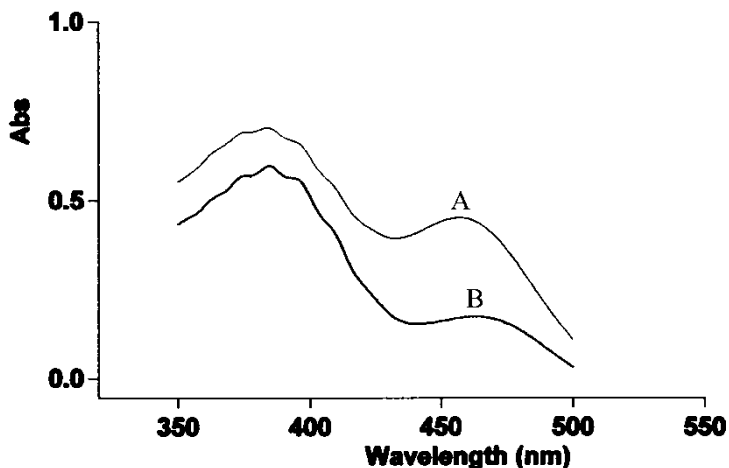
**Table 1.** Oxidative cleavage of alkenes to carboxylic acids by *cis*-[RuCl<sub>2</sub>(bipy)<sub>2</sub>]·2H<sub>2</sub>O/IO(OH)<sub>5</sub>

Substrate	Product	Yield (%) [TO]	Reaction time (h)
	Glutaric acid	85(170)	2
	Adipic acid	92(184)	2
	Suberic acid	75(150)	2
	Palmetic acid	80(160)	2
	Benzoic acid	90(180)	2
	Benzoic acid	90(180)	2
	Pentanoic acid	90(180)	2
	Hexanoic acid	80(160)	2
	Heptanoic acid	70(140)	2

Reaction conditions: alkene (2 mmol), catalyst (0.01 mmol), and periodic acid (10 mmol) were added to a mixture of CCl<sub>4</sub>:CH<sub>3</sub>CN:H<sub>2</sub>O (1:1:2 v/v), stirring at room temperature for 2 h. TO = turnover = moles of the product/moles of the catalyst.

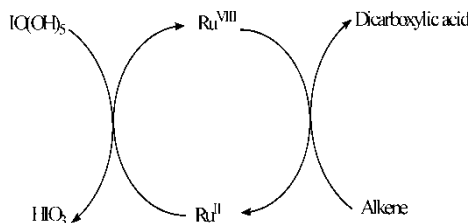
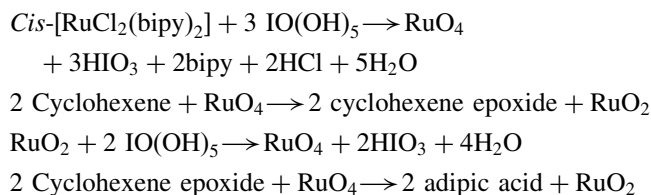
### NATURE OF THE ACTIVE SPECIES AND THE PROPOSED MECHANISM

Because the precise mechanistic study for reactions containing low-valent ruthenium complexes as catalysts suggests the formation of metal-oxo intermediates,<sup>[8]</sup> we investigated the nature of the active species responsible for the cleavage by carrying out the electronic spectrum for the reaction mixture without addition of the substrate. We found that the electronic spectra of both the aqueous and CCl<sub>4</sub> layers showed the characteristic peaks of RuO<sub>4</sub> with attendant vibrational fine structure at about 463 nm and 387 nm for the organic layer (curve A) and at about 475 nm and 390 nm for the aqueous layer (curve B) (Figure 1). Similar results were reported for the oxoruthenate complexes containing RuO<sub>4</sub>.<sup>[9]</sup>



**Figure 1.** Electronic spectrum of the catalyst system; *cis*-[RuCl<sub>2</sub>(bipy)<sub>2</sub>]·2H<sub>2</sub>O (0.01 mmol) and IO(OH)<sub>5</sub> (10 mmol) were added in a biphasic solvent system [CH<sub>3</sub>CN (5 cm<sup>3</sup>), CCl<sub>4</sub> (5 cm<sup>3</sup>), and H<sub>2</sub>O (10 cm<sup>3</sup>)] with stirring. The electronic spectrum of organic layer is A and the electronic spectrum of aqueous layer is B.

The oxidative cleavage of alkenes to acids by the present catalyst system is likely to proceed through a similar mechanism as that suggested for RuO<sub>4</sub>.<sup>[10]</sup> In this mechanism, the produced RuO<sub>4</sub> cleaves the alkene to acid and converted into RuO<sub>2</sub>, which in turn will be further oxidized to RuO<sub>4</sub> by excess IO(OH)<sub>5</sub> according to the following equations.



**Scheme 1.** Catalytic cycle for oxidative cleavage of alkenes to acids by *cis*-[RuCl<sub>2</sub>(bipy)<sub>2</sub>]·2H<sub>2</sub>O/IO(OH)<sub>5</sub>.

This catalytic cycle will continue until all the substrate is completely consumed (Scheme 1).

## CONCLUSION

We conclude that the complex *cis*-[RuCl<sub>2</sub>(bipy)<sub>2</sub>]·2H<sub>2</sub>O can be used as an effective catalyst for oxidative cleavage of alkenes to acids with IO(OH)<sub>5</sub> as a cooxidant at room temperature, and the active catalyst species seems to be RuO<sub>4</sub>. This procedure can eliminate our current need for the use of stoichiometric oxidants.

## EXPERIMENTAL

### Instrumentation and Chemicals

#### Instrumentation

The <sup>1</sup>H NMR spectra were made in CDCl<sub>3</sub> solutions on a high-resolution Bruker AM 300L spectrometer with tetramethylsilane (TMS) as internal standard at Cairo University. The infrared spectra were recorded on a Mattson 5000 FT-IR and the electronic spectra on a UV-visible vision software V 3.2 at Mansoura University. Microanalysis was carried out at Cairo University Microanalytical Unit.

#### Chemicals

All chemicals were obtained from Aldrich and used as received. The complex *cis*-[RuCl<sub>2</sub>(bipy)<sub>2</sub>]·2H<sub>2</sub>O was prepared using Sullivan's procedure.<sup>[11]</sup>

### Oxidative Cleavage of Alkenes

An alkene (2 mmol), *cis*-[RuCl<sub>2</sub>(bipy)<sub>2</sub>]·2H<sub>2</sub>O (0.01 mmol), and IO(OH)<sub>5</sub> (10 mmol) were added in a biphasic solvent system [CH<sub>3</sub>CN (5 cm<sup>3</sup>), CCl<sub>4</sub> (5 cm<sup>3</sup>), and H<sub>2</sub>O (10 cm<sup>3</sup>)] with stirring. The reaction mixture was stirred at room temperature for the times specified in Table 1. The products were extracted with diethylether (3 × 10 cm<sup>3</sup>), dried over MgSO<sub>4</sub>, and evaporated under reduced pressure.

### Large-Scale Oxidation of Styrene

Styrene (20 mmol) was added to a solution of CCl<sub>4</sub> (50 cm<sup>3</sup>), CH<sub>3</sub>CN (50 cm<sup>3</sup>), and H<sub>2</sub>O (100 cm<sup>3</sup>) containing IO(OH)<sub>5</sub> (100 mmol) and

*cis*-[RuCl<sub>2</sub>(bipy)<sub>2</sub>]·2H<sub>2</sub>O (0.1 mmol). The mixture was stirred at room temperature for 2 h. The product was isolated as described to give benzoic acid (19 mmol) (95% yield).

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