

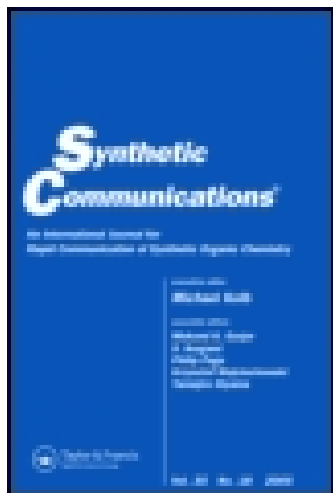
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### Catalytic Oxidative Cleavage of Electrophilic Double Bonds

Bingnan Huang <sup>a</sup>, Maksim Khrapov <sup>a</sup>, Keith C. Hansen <sup>a</sup>, John P. Idoux <sup>a</sup> & John T. Gupton <sup>b</sup>

<sup>a</sup> Department of Chemistry, Lamar University, Beaumont, TX, 77710

<sup>b</sup> Department of Chemistry, University of Central Florida, Orlando, FL, 32816

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CATALYTIC OXIDATIVE CLEAVAGE OF  
ELECTROPHILIC DOUBLE BONDS

Bingnan Huang, Maksim Khrapov,  
Keith C. Hansen\* and John P. Idoux

Department of Chemistry, Lamar University,  
Beaumont, TX 77710

and

John T. Gupton

Department of Chemistry, University of Central  
Florida, Orlando, FL 32816

**Abstract:** Oxidative cleavage of a variety of electro-  
philic double bond substrates has been effected under  
mild reaction conditions by sodium metaperiodate or  
sodium hypochlorite catalyzed by ruthenium oxide.

Catalytic oxidation is an extremely important  
industrial technology. For example, such technology  
probably accounts for the production of more tons of

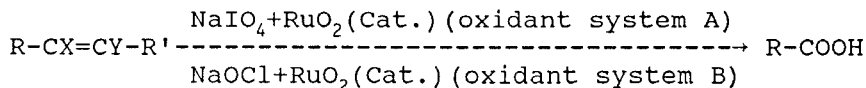
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\* To whom correspondence should be addressed.

bulk industrial chemicals than any other catalytic reaction.<sup>1</sup> On the other hand, many synthetic organic chemists still prefer more traditional oxidants for laboratory scale preparations. However, the use of a metal catalyst such as ruthenium tetraoxide in conjunction with a cheap, readily available oxygen source like oxygen,<sup>2</sup> hydrogen peroxide,<sup>3</sup> tert-butyl hydroperoxide,<sup>4</sup> sodium hypochlorite<sup>5</sup> or sodium metaperiodate,<sup>6</sup> offers the advantages of being economically attractive and environmentally friendly.

In conjunction with our interests in developing safe, inexpensive and effective processes for decomposition of unsaturated priority pollutants, the catalytic oxidative cleavage of electrophilic double bonds in some model compounds has been investigated. The reaction of some side-chain halosubstituted styrenes(halostyrenes) and of some double bond halosubstituted alkenes (haloalkenes) has been successfully carried out with sodium metaperiodate or sodium hypochlorite in the presence of catalytic amounts of ruthenium oxide as illustrated in Scheme 1. The results are summarized in Table 1 and 2, respectively.

In the initial study, halostyrene and haloalkene substrates were reacted with oxidant system A under



## 1

- a:** X=Y=R'=H, R=phenyl;      **h:** R=n-C<sub>8</sub>H<sub>17</sub>, X=Y=Cl, R'=H;  
**b:** Y=R'=H, X=Br, R=phenyl;    **i:** R=n-Bu, X=Br, Y=H, R'=i-Pr;  
**c:** X=Y=Br, R'=H, R=phenyl;    **j:** R=n-Bu, X=Br, Y=R'=H;  
**d:** X=Y=Cl, R'=H, R=phenyl;    **k:** R=n-Bu, Y=Br, X=R'=H;  
**e:** Y=R'=H, X=Cl, R=phenyl;    **m:** R=n-C<sub>8</sub>H<sub>17</sub>, X=Y=Br, R'=H;  
**f:** X=Y=H, R'=Br, R=phenyl;    **n:** R=n-C<sub>7</sub>H<sub>15</sub>, X=Y=Br, R'=CH<sub>3</sub>;  
**g:** R=n-C<sub>7</sub>H<sub>15</sub>, X=Y=Cl, R'=CH<sub>3</sub>;   **p:** R=R'=phenyl, X=Y=Cl.

## Scheme 1.

typical Sharpless conditions.<sup>7</sup> Oxidative cleavage of the double bonds in both types of substrate occurred smoothly to give the expected benzoic acid and carboxylic acids in excellent yields (Table 1). These results prompted us to consider oxidant system B, because sodium hypochlorite has a lower cost, lower toxicity and lower molecular weight per active oxygen than that of the sodium metaperiodate used in oxidant system A. Furthermore, to make the reaction more practicable, we attempted to use as little organic solvent as possible and to run the reaction at room temperature. Accordingly, in a well-stirred aqueous

**Table 1:** Oxidative double bond cleavage by sodium metaperiodate and catalytic amount of ruthenium oxide\*

Entry	Compound	Reaction Time (hrs)	Product	Isolated Yield (%)
1	<b>1a</b>	7.2	PhCOOH	86
2	<b>1b</b>	6	PhCOOH	90
3	<b>1c</b>	18	PhCOOH	80
4	<b>1d</b>	8	PhCOOH	86
5	<b>1e</b>	7	PhCOOH	82
6	<b>1f</b>	10	PhCOOH	91
7	<b>1g</b>	6	n-C <sub>7</sub> H <sub>15</sub> COOH	90
8	<b>1h</b>	6	n-C <sub>8</sub> H <sub>17</sub> COOH	93
9	<b>1i</b>	6	n-C <sub>4</sub> H <sub>9</sub> COOH i-C <sub>3</sub> H <sub>7</sub> COOH	85 75
10	<b>1j:1k=1:1#</b>	9	n-C <sub>4</sub> H <sub>9</sub> COOH	87
11	<b>1m</b>	11	n-C <sub>8</sub> H <sub>17</sub> COOH	88
12	<b>1n</b>	12	n-C <sub>7</sub> H <sub>15</sub> COOH	81
13**	<b>1g</b>	0.5	C <sub>7</sub> H <sub>15</sub> COCOCH <sub>3</sub>	89
14	<b>1p</b>	0.5	PhCOCOPh	97

\* Molar Ratio: Substrate : RuO<sub>2</sub> : NaIO<sub>4</sub> = 1.0 : 0.022 : 4.4

Solvent used: CH<sub>3</sub>CN : CH<sub>2</sub>Cl<sub>2</sub> : H<sub>2</sub>O = 3 : 3 : 2  
(volume ratio)

Reaction temperature: room temperature.

# molar ratio.

\*\* Molar ratio: **1g**: RuO<sub>2</sub>: NaIO<sub>4</sub> = 1.0: 0.022: 2.2.

suspension, in the absence of any organic solvent, the halostyrenes (**1a-1f**) were successfully transformed to the corresponding benzoic acids in excellent yields by oxidant system B; however, under the same conditions, the dihalosubstituted alkenes (**1g**, **1h** and **1n**) and monohalo-substituted alkenes (**1j** and **1k**) were converted to the corresponding carboxylic acids in poor yields (Table 2). When a small amount of acetonitrile was added to the haloalkene reaction system, the yields were improved significantly and monohaloalkenes with a terminal double bond gave much better yields than dihaloalkenes. Acetonitrile is believed to act as a cosolvent and/or a good ligand for ruthenium. Sodium metaperiodate<sup>7</sup> and sodium hypochlorite<sup>7,8</sup> have been reported to cleave both C-C double bonds in alkenes and aromatic rings in alkyl benzene or quinoline derivatives. Our results with the halostyrenes, which have an *exo* double bond and a benzene ring in the same molecule, indicate that even deactivated double bonds are cleaved much more easily than the aromatic ring.

In the reaction of 1,2-dichloro-1,2-diphenylethene (**1p**) with oxidant system A the final product was benzil (**7**), which can not be cleaved to give benzoic acid. In the reaction of 2,3-dichlorodecene-2 (**1g**) with oxidant

**Table 2:** Oxidative double bond cleavage by sodium hypochlorite and catalytic amount of ruthenium oxide\*

Entry	Compound Used	Cosolvent	Reaction Time(hrs)	Product	Yields (%)
1	<b>1e</b>	none	7	PhCOOH	82
2	<b>1d</b>	none	7	PhCOOH	83
3	<b>1c</b>	none	8	PhCOOH	82
4	<b>1f</b>	none	36	PhCOOH	60
5	<b>1f</b>	CH <sub>3</sub> CN	10	PhCOOH	80
6	<b>1b</b>	none	10	PhCOOH	85
7	<b>1b</b>	CH <sub>3</sub> CN	10	PhCOOH	90
8	<b>1n</b>	CH <sub>3</sub> CN	24	n-C <sub>7</sub> H <sub>15</sub> COOH	40
9	<b>1n</b>	none	25	n-C <sub>7</sub> H <sub>15</sub> COOH	13#
10	<b>1g</b>	CH <sub>3</sub> CN	28	n-C <sub>7</sub> H <sub>15</sub> COOH	45
11	<b>1g</b>	none	29	n-C <sub>7</sub> H <sub>15</sub> COOH	11#
12	<b>1h</b>	CH <sub>3</sub> CN	24	n-C <sub>8</sub> H <sub>17</sub> COOH	43
13	<b>1h</b>	none	16	n-C <sub>8</sub> H <sub>17</sub> COOH	14#
14	<b>1m</b>	CH <sub>3</sub> CN	25	n-C <sub>8</sub> H <sub>17</sub> COOH	46
15	<b>1j:1k=1:1**</b>	CH <sub>3</sub> CN	27	n-C <sub>4</sub> H <sub>9</sub> COOH	84
16	<b>1j &amp; 1k</b>	none	26	none	0

\* Substrate: NaClO: RuO<sub>2</sub>= 1.0: 4.0: 0.1-0.05 (molar)

H<sub>2</sub>O: CH<sub>3</sub>CN (when used)= 3:1-1.5 (volume)

Reaction temperature: room temperature.

\*\* in molar ratio.

# yields estimated by NMR.



system A the corresponding intermediate, decane-2,3-dione (**8**), was isolated in high yield(89%) when a molar ratio of 1g, sodium metaperiodate and ruthenium dioxide was 1.0:2.2:0.022, and the reaction was quenched by adding sodium bisulfite in shortened reaction times (<30 minutes).

The work presented above represents a potentially environmentally benign method to decompose haloalkene priority pollutants in aqueous systems. Additionally the results have possible uses as new synthetic methodology. The catalytic oxidation is an efficient means to convert vinyl halides to carbonyl function, and in some cases to convert alkynes to  $\alpha$ -diketones through the corresponding dihaloalkene.

#### Experimental

Melting and boiling points are uncorrected. IR spectra were obtained with a Perkin Elmer 710B spectrometer and only the important absorption bands are given.  $^1\text{H}$  NMR spectra were measured with a 250MHz Bruker AC-250 and a 90MHz Varian EM-390 NMR spectrometer and chemical shifts are reported in  $\delta$ = ppm using TMS as an internal standard. GC/MS were performed with a Hewlett Packard 5970/5890. All reagents from commercial sources are used as received.

The melting points or boiling points, infrared spectra, and NMR spectra of the products were compared to published values of authentic samples.

Typical reaction conditions are as follows:

**Oxidation of  $\beta$ -bromostyrene(1f) by oxidant  
system A**

To a three-necked flask equipped with a condenser, a dropping funnel and a magnetic stirring bar were added 5.0g (23.5mmole) of sodium metaperiodate, 22mg (0.14mmole) of ruthenium dioxide and 10mL of water. While stirring, a mixture of 1.0g (10mmole) of  $\beta$ -bromostyrene, 15mL of methylene chloride and 15mL of acetonitrile were added dropwise at room temperature in a period of 20 minutes. The mixture was stirred for 10 hr. at the same temperature and then extracted with methylene chloride (3x15mL). The combined organic phase was washed with dilute aqueous sodium bisulfite solution until colorless and then with water. After removal of the solvent the resulting solid was recrystallized from methylene chlorolide to give 0.60g (91 %) of benzoic acid (2).

2: mp. 122-123°C (lit. 122-123°C<sup>9</sup>),

IR(film):2900(m. br.), 1700(s),

NMR(CCl<sub>4</sub>):7.60(m, 3H), 8.20(d, 2H), 12.70(s, 1H).

Styrene(**1a**),  $\alpha$ -bromostyrene(**1b**),  $\alpha,\beta$ -dibromostyrene(**1c**),  $\alpha,\beta$ -dichlorostyrene(**1d**) and  $\alpha$ -chlorostyrene(**1e**) were oxidized in a similar manner to give benzoic acid(Table 1).

**Oxidation of 1,2-dibromodecene-1(**1m**) by  
oxidant system A**

To a flask equipped as above were added 1.49g (5.0 mmole) of 1,2-dibromodecene-1 (**1m**), 18mg (0.11 mmole) of ruthenium dioxide, 15mL of methylene dichloride and 15mL acetonitrile. While stirring, a mixture of 4.50g (21mmole) of sodium metaperiodate and 10mL water were added dropwise at room temperature. The resulting solution was stirred for 11 hr. and then worked-up as described above. Distillation under reduced pressure gave 0.70g (88%) of nonanoic acid (**3**) as a colorless liquid.

**3**: bp.148-150°C/20mmHg (lit. 150°C/20mmHg<sup>9</sup>),

IR(film): 3000(br.), 1710(s).

<sup>1</sup>H NMR(neat):0.83(t, 3H), 1.30, 1.90(m, 12H), 2.27 (t, 2H), 11.80(s, 1H).

In a similar manner 2,3-dichlorodecene-2 (**1g**), 1,2-dichlorodecene-1 (**1h**), 4-bromo-2-methyl-octene-3 (**1i**), isomer mixture(ca. 1:1 in molar ratio) of 2-bromohexene-1 (**1j**) and 1-bromohexene-1 (**1k**), 2,3-

dibromodecene-2 (**1n**) and 1,2-dichloro-1,2-diphenylethene (**1p**) were oxidized by oxidant system A to form octanoic acid (**4**), **3**, pentanoic acid (**5**) and 2-methylpropanoic acid (**6**), **5**, **4** and benzil (**7**), respectively.

**4**: bp. 138–140°C/23mmHg (lit.<sup>9</sup> 140°C/23mmHg),

IR(film): 3000(br.), 1700(s),

<sup>1</sup>H NMR(neat): 0.87(t, 3H), 1.30, 1.60(m, 10H), 2.28(t, 2H), 10.92(s, 1H).

**5**: bp: 181–184° (lit.<sup>9</sup> 185°C),

IR(film): 3000(br.), 1705(s),

<sup>1</sup>H NMR(neat): 1.06(t, 3H), 1.70(m, 4H), 2.48(t, 2H), 10.80(s, 1H).

**6**: bp. 151–153°C (lit.<sup>9</sup> 153–154°C),

IR(film): 3000(br.), 1700(s),

<sup>1</sup>H NMR(CCl<sub>4</sub>): 1.13(d, 6H), 2.45(m, 1H), 11.12(s, 1H).

**7**: mp 93°C (lit.<sup>9</sup> 95–96°C).

IR(film): 3030(m), 1640(s).

#### Oxidation of $\alpha$ -chlorostyrene(**1e**) by oxidant system B

To a flask were added a mixture of 1.38g (10 mmole) of  $\alpha$ -chlorostyrene (**1e**), 160mg (1 mmole) of ruthenium dioxide and 5 mL of water. To the stirring solution, 25mL(40 mmole) of 12% sodium hypochlorite

aqueous solution containing 0.80g (20 mmole) of sodium hydroxide were then added dropwise at room temperature in a period of 1hr. The resulting solution was stirred at the same temperature for an additional 7hr. To quench the reaction, a suspension of 2.08g of sodium bisulfite in 2mL of water was added. Approximately 2mL of concentrated hydrochloric acid were then added until the mixture was acidic. The resulting mixture was extracted with methylene chloride (3x15mL) and the combined organic phase was washed with dilute sodium bisulfite solution until totally colorless. The solvent was removed by flask evaporation until ca. 2.5mL of liquid remained, from which 1.0g (82%) of benzoic acid (2) was obtained as colorless crystals.

By similar procedures **1b**, **1c**, **1d** and **1f** were oxidized by oxidant system B to give all benzoic acid in 85, 82, 83 and 60% yields, respectively.

**Oxidation of 2,3-dichlorodecene-2 (1g) by  
oxidant system B**

To a flask were added a mixture of 320mg (2.0 mmole) of ruthenium dioxide, the first 17 mL portion from 50mL (80 mmole) of 12% sodium hypochlorite solution and 1.6g (40 mmole) of sodium hydroxide. A

solution of 4.18g (20mmole) of 2,3-dichlorodecene-2 (1g) in 20 mL of acetonitrile was added dropwise and the contents were stirred at room temperature for 2hr. Then the second portion of 17 mL of 12% sodium hypochlorite was added in 5 minutes and there was another 3hr. of stirring. Finally, the third 16mL was added and the solution stirred for an additional 24hr. After a similar work-up as described for 1e, vacuum disillation gave 1.3g (45%) of octanoic acid (4) as a colorless liquid.

In a similar way 1h, isomeric mixture of 1j and 1k, 1m and 1n were transformed to the corresponding carboxylic acids 3, 5, 5 and 4, respectively (Table 2).

#### **The preparation of decane-2,3-dione(8)**

A mixture of 2.09g (10mmole) of 2,3-dichlorodecene-2 (1g), 35mg (0.22mmole) of ruthenium dioxide, 20mL of methylene chloride and 20mL of acetonitrile were added into a flask while stirring, a solution of 4.6g (22mmole) of sodium metaperiodate in 15mL of water was added dropwise in 15 minutes. The resulting contents were stirred at room temperature for another 15 minutes and 1.04g (10mmole) of sodium bisulfite

was added to quench any further reaction. After a similar work-up, distillation under reduced pressure gave 1.5g(89%) of decane-2,3-dione (**8**) as pale yellow liquid.

**8**: bp. 93-95°C/16mmHg (lit.<sup>10</sup> 104-107°C/20mmHg),

IR(film): 1720(s),

<sup>1</sup>H NMR(neat): 0.87(t, 3H), 1.34(m, 10H), 2.21(s, 3H), 2.67(t, 2H).

MS: 170(8, M), 127(30), 57(100).

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