Electrooxidative Fission of Carbon–Carbon Double Bond in a $K_2OsO_2(OH)_4/HIO_4$ Double Mediatory System

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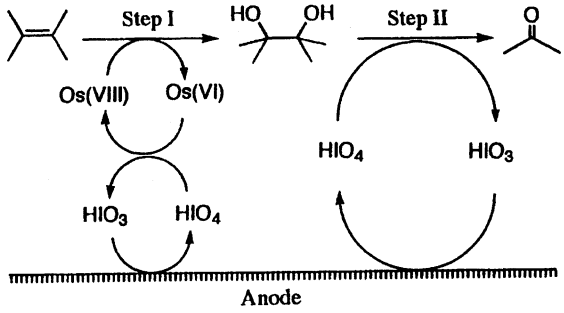
(Received May 11, 1995)

Electrooxidation of olefins in the presence of potassium osmate (0.04 molar amount) and periodic acid (0.5 molar amount) afforded the corresponding carbon–carbon double bond cleavage products in moderate to good yields, where the turnover number of periodic acid reached ca. 3.

The fission of carbon–carbon double bond with the combined use of osmium catalyst and periodate (Os/IO_4^-) is a potent alternative to ozone method.[1—3] The Os/IO_4^- system has, however, met limited numbers of applications in a large-scale reaction, since a large excess amount of periodate (5—6 molar amounts) is usually required to complete the reaction.[3] Meanwhile, indirect electrooxidation with recycle-use of oxidants has been intensively investigated and proved to be a promising tactics to reduce the amount of expensive or troublesome oxidants. Many efforts have been devoted to electrochemical production of periodate from the lower valent iodine compounds.[4—10] However, only a few indirect electrooxidations of organic molecules using periodate as a recyclable oxidant have appeared. Johnson et al., patented the electrooxidative fission of carbon–carbon double bond in the presence of osmium catalyst and 15 molar amounts of iodate.[11] The periodate-mediated electrooxidative fission of glycols with 2 molar amounts of iodate has been disclosed by Nonaka et al.[12—14] Recently, Steckhan and his co-workers have reported the electrooxidative fission of carbon–carbon double bond in a ruthenium oxometallate/iodate double mediatory system.[15] Most of the periodate-mediated electrooxidations have, however, been conducted in the presence of an excess amount of iodate salt (2—15 molar amounts) which undergoes two-electron oxidation leading to periodate in situ. To the best of our knowledge, recycle-use of a catalytic amount of periodate in electrooxidative media has not been realized. Herein, we describe the electrooxidative carbon–carbon double bond fission in the presence of catalytic amounts of potassium osmate (0.04 molar amount) and periodic acid (0.5 molar amount) affording the corresponding carbonyl compounds in moderate to good yields, in which dihydroxylation of olefins (step I) and subsequent carbon–carbon bond fission (step II) would proceed in the manner as illustrated in Scheme 1.



Scheme 1. Os/HIO_4 double mediatory electrooxidation of olefins.

Experimental

Materials. 3-Methyl-3-butenyl benzoate (**1**)[16] and citronellyl benzoate were prepared by esterification of the corresponding alcohols with benzoyl chloride in the presence of triethylamine in dichloromethane and purified by chromatography (SiO_2). Acetonitrile was distilled over diphosphorus pentaoxide under nitrogen and stored under nitrogen. Water was deionized and subsequently distilled. All other chemicals and solvents were used as supplied without further purification.

Instrumentation. NMR spectra were determined with a Varian VXR-200 (200 MHz for proton and 50 MHz for carbon-13). The ^1H NMR signals are expressed in ppm downfield from internal tetramethylsilane. The ^{13}C NMR signals are expressed in ppm using chloroform-*d* as a reference (77 ppm). IR spectra were obtained with a JASCO FT-IR-5000 spectrometer in wave number (cm^{-1}). Mass spectra were recorded with Hitachi M-80 double focusing mass spectrometer. High performance liquid chromatography (HPLC) was executed with Hitachi HPLC instrument equipped with L-6000 LC pump, L-4000 UV detector, and 833A integrator.

General Procedure. Electrolysis was carried out in a Nafion®-separated H-type divided cell fitted with β-PbO_2 anode (1.5×1.5 cm^2)[17] and platinum cathode (1.5×2.0 cm^2). Into both the anode and cathode compartments was charged a solution of tetraethylammonium *p*-toluene-

sulfonate (150 mg, 0.50 mmol, each) in acetonitrile (7.5 ml, each) containing water (2.2 ml, each). Into the anode compartment, an olefinic substrate (0.55 mmol), potassium osmate dihydrate (7.4 mg, 0.02 mmol), and periodic acid dihydrate (60 mg, 0.27 mmol) were added. The mixture was electrolyzed at a constant current density (typically 6.7 mA cm^{-2}) under stirring at room temperature until most of the substrate was consumed. The yield of each of the products was determined by HPLC.[18] The products were isolated by column chromatography (SiO_2, hexane/ethyl acetate: 10/1—1/1) and characterized by ^1H NMR, ^{13}C NMR, IR, and MS Spectra. The representative results are compiled in Tables 1, 2, and 3.

Oxidation of 3-Methyl-3-butenyl Benzoate (1) in 4.2 mmol Scale. Electrolysis was carried out in a Nafion®-separated H-type divided cell fitted with β-PbO_2 anode (1.5×3.0 cm^2)[17] and platinum cathode (1.5×2.0 cm^2). Into both the anode and cathode compartments was charged a solution of tetraethylammonium *p*-toluenesulfonate (1.2 g, 4.0 mmol, each) in acetonitrile (60 ml, each) containing water (18 ml, each). Into the anode compartment, 3-methyl-3-butenyl benzoate (**1**, 803 mg, 4.2 mmol), potassium osmate dihydrate (62 mg, 0.17 mmol), and periodic acid dihydrate (480 mg, 2.1 mmol) were added. The mixture was electrolyzed at a constant current density (5.6 mA cm^{-2}) for 22.5 h (5 F mol^{-1}) under stirring at room temperature. The anolytes were concentrated under reduced pressure. The residue was taken up with ethyl acetate and subsequently washed with water, 5% sodium hydrogen sulfite, saturated sodium hydrogen carbonate, and brine. The organic layer was separated and dried over anhydrous magnesium sulfate. After evaporation of the solvents, the residue was chromatographed (SiO_2, hexane/ethyl acetate: 10/1—1/1) to give 3-oxo-3-butyl benzoate (**3**) (677 mg, 83%).

3,4-Dihydroxy-3-methylbutyl Benzoate (2):[19] IR (neat) 3424, 2971, 1716, 1451, 1316, 1278, 1115 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.28 (s, 3H), 1.89—2.13 (m, 2H), 3.44—3.61 (dd, J=11.0, 16.7 Hz, 2H), 4.51 (t, J=6.4 Hz, 2H), 7.39—7.61 (m, 3H), 7.98—8.09 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=23.58, 36.89, 61.53, 69.83, 72.04, 128.38, 129.47, 129.98, 133.04, 205.73; SIMS (glycerin) m/z (rel intensity) 225 ($(M+1)^+$; 100).

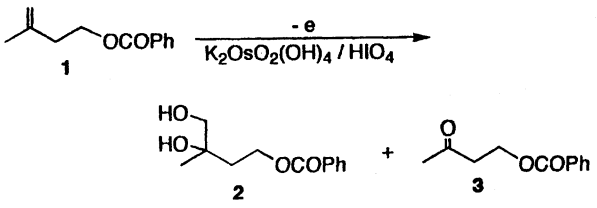
3-Oxobutyl Benzoate (3):[20] IR (neat) 2980, 1720, 1602, 1372, 1278, 1170, 1115 cm^{-1}; ^1H NMR ($CDCl_3$) δ= 2.24 (s, 3H), 2.91 (t, J=6.4 Hz, 2H), 4.59 (t, J=6.4 Hz, 2H), 7.35—7.61 (m, 3H), 7.91—8.08 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=14.16, 30.29, 42.35, 59.81, 128.24, 129.55, 130.11, 133.04, 205.73.

6-Benzoyloxy-4-methylhexanal: IR (neat) 3064, 2960, 2721, 1724, 1602, 1585, 1453, 1389, 1315, 1278, 1177, 1113, 1071, 1026, 953, 713, 688, 676 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.99 (d, J=6.1 Hz, 3H), 1.45—1.90 (m, 5H), 2.49 (m, 2H), 4.37 (m, 2H), 7.40—7.60 (m, 3H), 8.00—8.35 (m, 2H), 9.79 (t, J=1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=19.17, 28.74, 29.59, 35.31, 41.51, 63.06, 128.34, 129.49, 130.29, 132.88, 166.59, 202.38. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74%. Found: C, 71.55; H, 7.80%.

Results and Discussion

Firstly, a mixture of 3-methyl-3-butenyl benzoate **1** (0.5 mmol), potassium osmate dihydrate (0.04 molar amount), and periodic acid dihydrate (0.5 molar amount) in acetonitrile and water (10:3 v/v) containing tetraethylammonium *p*-toluenesulfonate (0.05 mol dm^{-3}) was electrolyzed at a constant current density of 6.7 mA cm^{-2} at room temperature. After passage of 5 F mol^{-1} (1 F≈96500 coulomb) of electricity, HPLC of the products revieled that 91% yield of 3-oxobutyl benzoate (**3**) was formed together with a small amount of 3,4-dihydroxy-3-methylbutyl benzoate (**2**) (6%)[21] (Scheme 2 and Entry 1 in Table 1). The Os/IO_4^--mediated electrooxidation of **1** in a larger scale (4.2 mmol) was similarly performed to give the ketone **3** in 83% yield, suggesting that the scale up of the electrooxidation of **1** into **3** would be achieved without difficulties.

The course of the oxidation of olefin **1** was followed by HPLC, suggesting that the carbon-carbon double bond fission proceeds through dihydroxylation of olefin **1** and subsequent glycol cleavage reaction (Fig. 1). In the ini-



Scheme 2. Electrooxidation of olefin **1**.

Table 1. Oxidation of Olefin **1** and Diol **2**

Entry	Substrate	$K_2OsO_2(OH)_4$	HIO_4	Electricity	Yield/%[a]		Recovery/%[a,b]
		Molar amount	Molar amount	F mol^{-1}	**2**	**3**	**1**
1	**1**	0.04	0.5	5.0	6	91	n.d.
2	**1**	—	—	5.0	2	8	85
3	**1**	—	0.5	5.0	15	9	70
4	**1**	0.04	—	5.0	16	33	38
5[d]	**1**	0.04	—	5.0	15	34	31
6	**1**	0.04	0.5	—	72	10	n.d.
7[d]	**2**	—	—	4.0	5[c]	89	—
8	**2**	—	—	4.0	75[c]	11	—

a) Determined by HPLC. b) n.d.=not detected. c) Recovery. d) Sulfuric acid (0.25 molar amout) was added into the anodic solution.

Table 2. Effects of the Amount of HIO_4 and Current Density in the Electrooxidation of **1**[a)]

Entry	HIO_4 Molar amount	Current density / mA cm^{-2}	Yield/%[b)] **2**	**3**
1	0.5	6.7	6	91
2	0.3	6.7	16	74
3	0.1	6.7	65	22
4	0.05	6.7	46	31
5	0.5	4.4	5	89
6	0.5	8.9	19	68
7	0.5	13	64	18

a) 5 F mol^{-1} of electricity was passed. b) Determined by HPLC.

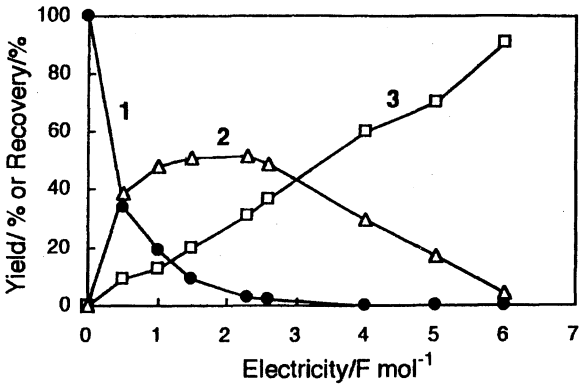


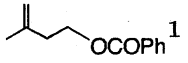
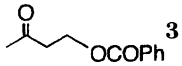
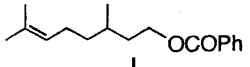
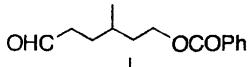
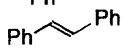
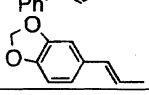
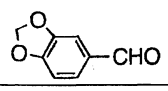
Fig. 1. The course of electrooxidation of olefin **1**.

tial stage of the reaction, the dihydroxylation of olefin **1** mainly occurred while a small part of thus formed diol **2** suffered further oxidation leading to ketone **3**. Subsequently, the oxidative fission of the diol **2** into **3** took place and mostly completed after passage of 6 F mol^{-1} of electricity.

Next, the roles of the osmium catalyst and periodic acid in the electrooxidation were examined. The direct electrooxidation of the olefin **1** in the absence of the osmium catalyst and periodic acid gave only a small amount of ketone **3** (8%) (Entry 2 in Table 1). In the presence of periodic acid alone, the electrooxidation of **1** gave only 9% yield of the ketone **3** (Entry 3 in Table 1). On the other hand, in the presence of the osmium catalyst alone, the ketone **3** was obtained in 33% yield (Entry 4 in Table 1). The yield of **3** was not affected by the addition of sulfuric acid (0.25 molar amount) (Entry 5 in Table 1). These results indicate that the presence of both the osmium catalyst and periodic acid is indispensable for the efficient carbon–carbon double bond fission of the olefin **1**. The oxidation of the olefin **1** in the same media as employed in Entry 1 without passing electricity was also carried out to give the diol **2** in 72% together with a small amount of ketone **3** (Entry 6 in Table 1). This fact indicates that iodate (IO_3^-) as well as periodate (IO_4^-) does work as a co-oxidant for osmium-catalyzed dihydroxylation. Indeed, the oxidation of **1** with potassium iodate (0.5 molar amount) without passing electricity afforded the diol **2** in 48%, but no detectable amount of ketone **3**.

Above all, the high yield of ketone **3** in the electrooxidation of **1** (Entry 1 in Table 1) can be attributed to oxidation of the electrochemically regenerated periodic acid which works as an oxidant for either regeneration of osmate or glycol cleavage. On the basis of the fact that two molar amounts of periodic acid must be required for the oxidative cleavage of olefinic bond, the turnover number of periodic acid is estimated to be ca. 3. The direct electrooxidation of the diol **2** into the ketone **3** would competitively occur in the present Os/IO_4^--mediated electrolysis. The electrochemical cleavage of the diol **2** occurred preferably in an acidic media; thus, the electrooxidation of the diol **2** in the presence of sulfuric acid (0.25 molar amount, pH 1.2) gave the ketone **3** in 89% yield whereas in a neutral condition only 11% yield of ketone **3** was formed (Entries 7 and 8 in Table 1). The pH value of the anolyte of the Os/IO_4^--

Table 3. Electrooxidation of Olefins in the $K_2OsO_2(OH)_4/HIO_4$ Double Mediatory System[a)]

Entry	Substrate	Product	Electricity / F mol^{-1}	Yield/%[b)]
1	 **1**	 **3**	5	91
2			10	72
3			7	71
4			9	94
5		PhCHO	8	66
6			2.5	62[c)]

a) Conditions: substrate 0.55 mmol, $K_2OsO_2(OH)_4$ 0.04 molar amount, HIO_4 0.5 molar amount, CH_3CN/H_2O (10/3 v/v) 9.7 ml (each compartment), Et_4NOTs 0.05 mol dm^{-3}, (β-PbO_2)-(Pt), Nafion®-separated divided cell, 6.7 mA cm^{-2}, r.t. b) Determined by HPLC. c) Isolated.

mediated electrooxidation of **1** varied from pH 1.0 to 0.8 during the course of the electrolysis (Entry 1 in Table 1). Therefore, it can be reasonably assumed that the direct electrooxidation of the intermediary diol **2** into **3** partly perticipates to the efficient formation of **3**.

Further reduction of the amount of periodic acid was attempted in the electrooxidation of olefin **1** (Entries 1, 2, 3, and 4 in Table 2). The decrease of the amount of periodic acid (less than 0.5 molar amount) resulted in the decrease of the yield of the ketone **3**. This fact suggests that the regeneration of periodic acid from iodic acid is not so efficient as to promote the dihydroxylation and/or the glycol cleavage smoothly. Indeed, the anolyte gradually turned to brown during the electrolysis probably due to the formation of iodine molecule resulting from some reductive degradation of iodate ion. The lability of iodine species, i.e. iodate, in the electrolysis media seems to be responsible for the low turnover number of periodic acid.

The current density also affected the formation of ketone **3** (Entries 1, 5, 6, and 7 in Table 2). Thus, the electrolysis at the current density of 4.4 and 6.7 mA cm^{-2} lead to the ketone **3** in good yield (89 and 91%, respectively) whereas at higher current density, e.g. 8.9 and 13 mA cm^{-2}, considerable decrease of the efficiency of the formation of the ketone **3** was observed.

The Os/IO_4^--mediated electrooxidation method was successfully applied to a range of olefins (Table 3). The corresponding carbonyl compounds were obtained in moderate to good yields. The ketones were more preferably obtained in the indirect electrooxidation than the aldehydes. The electricity required for completion of each of the reactions varied in a range 2.5–10 F mol^{-1}, presumably because overoxidations of the desired carbonyl products and the eliminated counter parts, e.g. formaldehyde and acetaldehyde, oxidation of the solvents, etc. would competitively take place.

Conclusion

The carbon–carbon double bond fission was effectively achieved by indirect electrooxidation with potassium osmate (0.04 molar amount) and periodic acid (0.5 molar amount) affording the corresponding carbonyl compounds in moderate to good yields. The oxidative fission proceeded through dihydroxylation of olefin and subsequent glycol cleavage. High selectivity of ketone formation suggests that the regeneration of periodic species can occur in this electrooxidative media. The turnover number of periodic acid reached ca. 3. This is the first example of the electrochemical recycle-use of periodic acid.

The present work was supported by The Grant-in-Aid for Scientific Research Nos. 05235107, 05403025, and 06453140 from the Ministry of Education, Science and Culture. We are grateful to the 200 MHz SC-NMR laboratory of Okayama University for experiments.

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17) β-PbO_2/Ti (mesh) anode made by Japan Carlit Co., Ltd. was used.

18) The condition of HPLC analysis was as follows: column YMC-Pack AM-312 ODS (6.0 mmϕ×150 mm), mobile phase CH_3CN/H_2O 65 : 35, flow rate 1.0 ml min^{-1}, detection UV 254 nm. External standard method was employed for determination of products and substrates.

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21) The diol **2** was contaminated with a small amount of 2,4-dihydroxy-2-methylbutyl benzoate: IR (neat) 3384, 2975, 1716, 1451, 1277 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.39 (s, 3H), 1.74—2.06 (m, 2H), 3.87—4.07 (m, 2H), 4.29 (s, 2H), 7.40—7.65 (m, 3H), 8.00—8.12 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=24.48, 38.89, 59.14, 71.10, 72.58, 128.37, 129.55, 129.66, 133.16, 166.56; FDMS *m/z* (rel intensity) 225 ($(M+1)^+$; 100); MS (70 eV) *m/z* (rel intensity) 179 (2), 122 (45), 105 (100).