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Indirect Electrooxidation of Alcohols and Aldehydes by Using a Double Mediatory System Consisting of RuO_4/RuO_2 and Cl^+/Cl^- Redoxes in an Aqueous-Organic Two-Phase System

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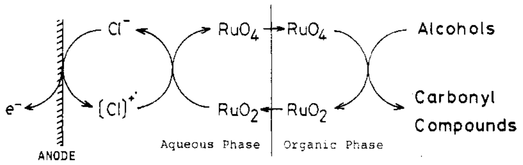
A double mediatory system consisting of RuO_4/RuO_2 and Cl^+/Cl^- redox couples has been developed for the indirect electrooxidation of alcohols and aldehydes. The reaction proceeds in the following manner: (1) oxidation of the substrate with ruthenium tetraoxide (RuO_4) in the organic layer, (2) regeneration of ruthenium tetraoxide from ruthenium dioxide (RuO_2) with active chlorine species (Cl_2 or $[Cl]^+$), and (3) oxidation of chloride ion to $[Cl]^+$ on the anode in the aqueous layer. The range of applicability of the present procedure is discussed by oxidations of (1) secondary alcohols to ketones, (2) primary alcohols and aldehydes to carboxylic acids, (3) 1,*n*-diols to lactones and keto acids, and (4) carbohydrate derivatives.

Oxidation of alcohols to carbonyl compounds is a reaction of preeminent importance in synthetic organic chemistry,[1] and, from an environmental point of view, considerable attention has recently been focused on the development of convenient and inexpensive oxidation methods[2] without resorting to a stoichiometric amount of metal reagents such as chromic acid and permanganate ion.[3] In this respect the electrooxidation method is currently a subject of intensive research.[4] However, due to the inherent high oxidation potential of the hydroxyl group,[5] direct electrooxidation has not shown any success. A variety of indirect procedures have therefore been devised by utilizing appropriate organic and inorganic chemicals as mediators (electron carriers).[6] However, some of the reported indirect electrooxidations are rather insufficient when applied to large-scale operation due to their low efficiencies with respect to (1) high turnover (catalytic recycles) and structural stability of the mediator, (2) facile electron transfer to the mediator, (3) rapid oxidation of the substrate with the mediator, and (4) easy separation of product from the mediator. We report here a facile ruthenium tetraoxide (RuO_4)[7] mediated electrooxidation of alcohols and aldehydes employing a two-phase system consisting of an organic solvent and aqueous sodium chloride solution. This allows for the separation of electron-transfer and chemical reaction processes in an in-cell method for strict exclusion of the contact of the substrate and product with electrodes.

Scheme I



It is known that ruthenium tetraoxide is a multipurpose oxidizing agent[8,9] and is soluble in organic solvents, whereas ruthenium dioxide, which is a reduced form of ruthenium tetraoxide, is insoluble and disperses in the aqueous layer of an aqueous–organic two-phase system. We have found that ruthenium dioxide suspended in the aqueous phase can be instantaneously oxidized to ruthenium tetraoxide by the electrolysis in sodium chloride solution.[7] Accordingly, as depicted in Scheme I, the present electrolysis process recycles in three reaction steps which involves (1) oxidation of alcohols by ruthenium tetraoxide in the organic phase, (2) regeneration of ruthenium tetraoxide from ruthenium dioxide by the action of active chlorine species (Cl_2 or $[Cl]^+$)[10] in an aqueous phase, and (3) electrooxi-

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(2) The following nonmetallic oxidizing reagents have recently been explored. $NaBrO_2$–AcOH: (a) Kageyama, T.; Ueno, Y.; Okawara, M. *Synthesis* **1982**, 815. (b) Kageyama, T.; Kawahara, S.; Kitamura, K.; Ueno, Y.; Okawara, M. *Chem. Lett.* **1983**, 1097. NaOCl–AcOH: (c) Stevens, R. V.; Chapman, K. T.; Weller, H. N. *J. Org. Chem.* **1980**, *45*, 2030. $Ca(OCl)_2$–AcOH: (d) Nwaukwa, S. O.; Keehn, P. M. *Tetrahedron Lett.* **1982**, *23*, 35, 3131. Oxoaminium salts: (e) Rozantsev, E. G.; Sholle, V. D. *Synthesis* 1971, 401. (f) Miyazawa, T.; Endo, T.; Shiihashi, S.; Okawara, M. *J. Org. Chem.* **1985**, *50*, 1332.

(3) Kauffman, J. M.; McKee, J. R. *J. Chem. Ed.* **1982**, *59*, 862.

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(6) Mediators previously reported is as follows. Bromide: (a) Pletcher, D.; Tomov, N. *J. Appl. Electrochem.* **1977**, 501. (b) Yoshida, J.; Nakai, R.; Kawabata, N. *J. Org. Chem.* **1980**, *45*, 5269. Iodide: (c) White, D. A. *J. Electrochem. Soc.* **1977**, *124*, 1177. (d) Shono, T.; Matsumura, Y.; Hayashi, J.; Mizoguchi, M. *Tetrahedron Lett.* **1979**, 165. Nitrate ion: (e) Leonard, J. E.; Scholl, P. C.; Steckel, T. P.; Lentsch, S. E.; Van De Mark, M. R. *Ibid.* **1980**, *21*, 4695. Sulfide: (f) Shono, T.; Matsumura, Y.; Mizoguchi, M.; Hayashi, J. *Ibid.* **1979**, 3861; (g) **1980**, *21*, 1867. *N*-Hydroxylamine: (h) Semmelhack, M. F.; Chou, C. S.; Cortes, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 4492. *N*-Hydroxyphthalimide: (i) Masui, M.; Ueshima, T.; Ozaki, S. *J. Chem. Soc., Chem. Commun.* **1983**, 479. Nickel hydroxide: (j) Kaulen, J.; Schäfer, H. J. *Tetrahedron* **1982**, *38*, 3299. Ruthenium complex: (k) Moyer, B. A.; Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2310. (l) Thompson, M. S.; De Giovani, W. F.; Moyer, B. A.; Meyer, T. J. *J. Org. Chem.* **1984**, *49*, 4972.

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(9) In a catalytic procedure, RuO_4 is generated in situ by using the following chemicals as a stoichiometric oxidant. $NaIO_4$: (a) Caputo, J. A.; Fuchs, R. *Tetrahedron Lett.* **1967**, 4729. (b) Lawton, B. T.; Szarek, W. A.; Jones, J. K. N. *Carbohydr. Res.* **1969**, *10*, 456. (c) Gopal, H.; Adams, T. *Tetrahedron* **1972**, *28*, 4259. NaOCl: (d) Wolfe, S.; Hasan, S. K.; Campbell, J. R. *J. Chem. Soc. D* **1970**, 1420. $BaBrO_3$: (e) Berkowitz, L. M.; Rylander, P. N. *J. Am. Chem. Soc.* **1958**, *80*, 6682. (f) Yamamoto, Y.; Suzuki, H.; Moro-oka, Y. *Tetrahedron Lett.* **1985**, *26*, 2107. H_2O_2: (g) Mitui Petrochemical Industries Ltd. Jpn Kokai Tokkyo Koho 80 102 528, 1981; *Chem. Abstr.* **1981**, *94*, 46774z. AcOOH: (h) Sheng, M. N. U.S. Patent 3 997 578, 1977; *Chem. Abstr.* **1977**, *86*, 105956v. (i) Ketcha, D. M.; Swern, D. *Synth. Commun.* **1984**, *14*, 915. $Pb(OAc)_4$: (j) Nakata, H. *Tetrahedron* **1963**, *19*, 1959. $K_2S_2O_8$: (k) Schröder, M.; Griffith, W. P. *J. Chem. Soc., Chem. Commun.* **1979**, 58. (l) Johnson, Matthey Inc. Jpn Kokai Tokkyo Koho 80 85 527, 1981; *Chem. Abstr.* **1981**, *94*, 46252c. $K_3Fe(CN)_6$: (m) Singh, L. P.; Singh, R. P. *J. Indian Chem. Soc.* **1981**, *58*, 1204.

(10) $[Cl]^+$ denotes the positive chlorine species anodically generated from chloride ion. For the anodic oxidation of chloride ion: Dotson, R. L.; Lynch, R. W. *J. Electrochem. Soc.* **1981**, *128*, 798.

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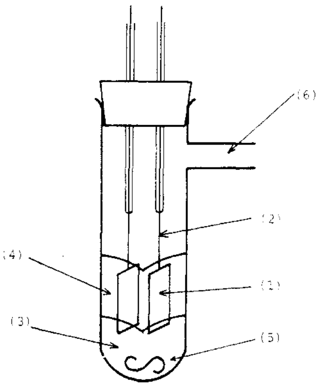

Figure 1. Small-scale electrolysis cell for a constant current electrolysis (undivided): (1) anode and cathode (platinum, 1.5 × 2.0 cm); (2) platinum wire; (3) organic phase; (4) aqueous phase; (5) stirring bar; (6) gas outlet.

dation of chloride ion to reactive chlorine species on the anode.

It is one of the purposes of this investigation to evaluate the scope and limitation of this indirect electrooxidation by studying (1) oxidation of secondary alcohols to ketones, (2) oxidation of primary alcohols and aldehydes to carboxylic acids, (3) oxidation of 1,*n*-diols to lactones and keto acids, and (4) oxidation of carbohydrate derivatives. A study of the reactivity of primary and secondary hydroxyls to the oxidants under a preparative electrolysis conditions was also undertaken.

Results

Oxidation of Secondary Alcohols to Ketones. Indirect electrooxidation of secondary alcohols to ketones has been attempted in a two-phase solution consisted of carbon tetrachloride and aqueous sodium chloride using platinum foil electrodes immersed in the upper aqueous phase in an undivided cell. For example, the electrolysis of 4-*tert*-butylcyclohexanol (**1**, 1.0 mmol) in a CCl_4 (5 mL)–saturated NaCl (buffered at pH 4 with 0.2 M NaH_2PO_4, 10 mL) system in the presence of $RuO_2 \cdot 2H_2O$ (3 mg, 0.02 mmol) at a current of 20 mA/cm^2 (applied voltage: 2.0–3.0 V) afforded 4-*tert*-butylcyclohexanone (**2**) in 93% yield by passing 2.4 F/mol of electricity (for about 64 min). We have encountered no difficulties in scaling up the above procedure to 10–15-mmol scales by using the same reaction medium (CCl_4 (5 mL)–saturated NaCl (pH 4, 10 mL)–$RuO_2 \cdot 2H_2O$ (3–8 mg)) in the electrolysis cell shown in Figure 1 to give approximately identical chemical yields. In large-scale experiments (about 100–150-mmol scale), the electrolysis was carried out by using a circulating flow cell (Figure 2), in which the electrolyte was circulated at a linear rate of about 10 cm/s and most of the $RuO_2 \cdot 2H_2O$ employed was recovered by filtration.

The effect of halide salts in the aqueous layer was first examined in order to elucidate the optimum conditions. As shown in Table I, entries 1–7, satisfactory yields and current efficiencies were obtained when LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$ were employed as electron carriers for the oxidation of ruthenium dioxide to ruthenium tetraoxide. Ammonium chloride, however, did not work as well as was expected (entry 9). Both 0.5% HCl and sodium bromide afforded good results in producing **2** but were less efficient in their current efficiencies (entries 8 and 10). It should be noted that sodium iodide and potassium fluoride were not effective at all under the same electrolysis conditions (entries 11 and 12).

In addition, the concentration of sodium chloride (NaCl) and the pH in the aqueous layer were found to be important with respect to the conversion yield and current efficiency. As shown in Figure 3, in which the yield of **2** vs. the pH of the aqueous solution under various sodium chloride concentrations is plotted, saturated sodium chloride (ca. 23% solution) is of more advantage than low sodium chloride concentration and the current efficiency reaches a maximum at pH 4. Furthermore, the current density in the course of electrolysis affects the current efficiency. The plots of electricity required for the complete conversion of **1** to **2** under various current densities are shown in Figure 4, indicating that a current maintained at about 20 mA/cm^2 seems to be preferable for producing the desired **2**.

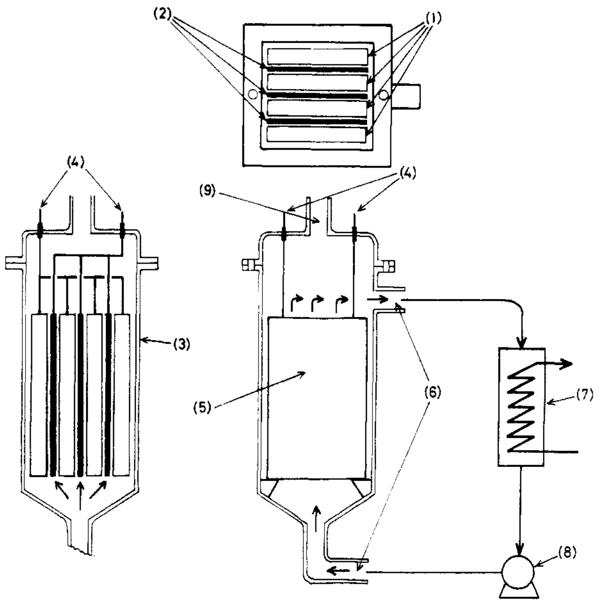

Figure 2. Schematic drawing of a circulating flow cell for a constant current electrolysis: (1) anode (graphite plates, 59 × 29 × 5 mm); (2) cathode (stainless gauze, 59 × 29 × 0.5 mm); (3) polypropylene vessel (ca. 14 × 4.5 × 4 cm); (4) anode and cathode terminal; (5) electrode plates; (6) electrolyte inlet and outlet; (7) heat exchanger with cooling water; (8) circulating pump; (9) gas outlet.

Table I. Effect of Halide Salt in the Oxidation of 4-*tert*-Butylcyclohexanol (1) to 2[a]

entry	halide salt (electrolyte)	electricity,[b] F/mol	product yield, %[c] **2**	product yield, %[c] **1**
1	LiCl	2.6	91	
2	NaCl	2.4	92	
3	NaCl[d]	2.4	93	
4	NaCl[e]	2.4	88	
5	KCl	2.4	90	
6	$MgCl_2$	2.6	91	
7	$CaCl_2$	2.9	88	
8	HCl[f]	7.2	91	
9	NH_4Cl	17.9	21	63
10	NaBr	5.3	90	
11	NaI	14.8		93
12	KF	19.2		92

[a] Unless otherwise noted, electrooxidations were performed at room temperature, using **1** (1 mmol), $RuO_2 \cdot 2H_2O$ (3 mg, 0.02 mmol) in CCl_4 (5 mL)–aqueous 15% halide salt solution (10 mL) buffered at pH 4 with 0.2 M NaH_2PO_4. [b] Consumed electricity based on **1**. [c] Yields based on isolated products. [d] Saturated solution (ca. 23%) was used. [e] Neutral solution (pH 7) was used. [f] 0.5% solution was used.

Sharpless et al. reported that ruthenium tetraoxide catalyzed oxidation of a variety of organic substrates could be greatly improved in a mixed solvent of MeCN–CCl_4–H_2O (2/2/3 v/v/v) system using sodium metaperiodate as a stoichiometric oxidant.[11] The electrooxidation

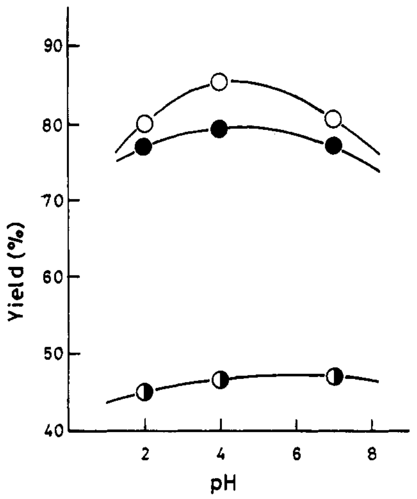

Figure 3. Relationships between the yield of **2** vs. pH of the aqueous phase under various sodium chloride concentrations. Electrolyses of **1** were carried out similarly as described in the Experimental Section and the products were isolated after passing 2.0 F/mol of electricity: (○) aqueous saturated NaCl, (●) aqueous 5% NaCl, (◑) aqueous 0.5% NaCl.

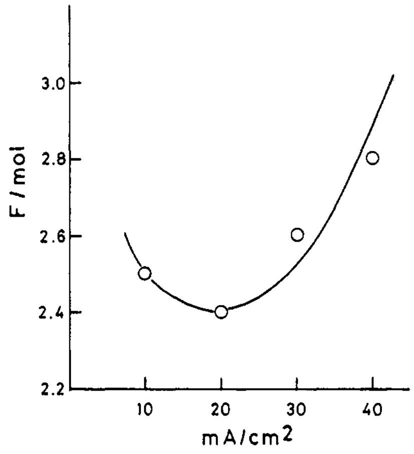

Figure 4. Plots of electricity required for complete conversion of **1** into **2** under various current densities. Electrolyses were performed using **1** (1.0 mmol) and $RuO_2 \cdot 2H_2O$ (0.02 mmol) in CCl_4 (5 mL)-saturated NaCl (buffered at pH 4 with 0.2 M NaH_2PO_4, 10 mL)-Pt system.

of **1** in the same media, however, proceeds much slower compared with CCl_4-H_2O (1/2 v/v) system and required 5.5 F/mol of electricity to complete the conversion. After examining a variety of solvent systems (Table II), we have found that a two-phase system consisting of CCl_4-H_2O (1/2 v/v) is the best choice for the electrooxidation of **1**. However in the cases where the alcohol was miscible with water, the electrolysis can be carried out in aqueous sodium chloride without using carbon tetrachloride to give high yields of the oxidized material (Table III, entries 12–15).

Several other ruthenium compounds, i.e., $RuCl_3 \cdot (H_2O)_x$, $Ru_3(CO)_{12}$, and $RuCl_2(Ph_3P)_3$ were also found to be useful in the electrooxidation of **1**. The results including electricity required for complete conversion of **1** to **2** and yield of **2** obtained by using the above ruthenium compounds under the electrolysis conditions of entry 3 (Table I) are as follows: $RuCl_3 \cdot (H_2O)_x$ (2.4 F/mol, 91%); $Ru_3(CO)_{12}$ (2.4 F/mol, 91%); $RuCl_2(Ph_3P)_3$ (2.5 F/mol, 92%).

The procedure described here is applicable for oxidation of a variety of aliphatic and aromatic secondary alcohols.

Table II. Electrooxidation of 1 in Various Organic Solvent-Saturated NaCl Systems[a]

entry	organic solvent-H_2O (satd NaCl) (v/v)	F/mol	yield of **2**, %[b]
1	CCl_4-H_2O (1/2)	2.4	93
2	$CHCl_3$-H_2O (1/2)	8.8	87
3	CH_2Cl_2-H_2O (1/2)	6.0	91
4	AcOEt-H_2O (1/2)	3.6	91
5	acetone-H_2O (1/2)	3.6	91
6	hexane-H_2O (1/2)	4.4	92
7	CH_3CN-H_2O (1/2)	8.3	91
8	CCl_4-CH_3CN-H_2O (2/2/3)	5.5	91

[a] Carried out using **1** (1.0 mmol) and $RuO_2 \cdot 2H_2O$ (0.02 mmol) with platinum electrodes in an undivided cell. [b] Based on isolated products.

Examples carried out under the conditions of entries 3 and 4 in Table I are summarized in Table III (entries 1–15). Methyl ketones are formed without undergoing a subsequent haloform reaction (entries 1 and 2). Oxidations of hydroxyl groups at the benzylic position proceed without any change at the benzene nucleus, giving the corresponding phenyl ketones (entries 8 and 9). The potentiality of the present procedure as a practical oxidation method is demonstrated by the oxidation of cyclohexane-1,4-diol to the corresponding diketone, a key intermediate in the commercial synthesis of 7,7,8,8-tetracyanoquinodimethane (TCNQ)[12] (entry 12). Both cis and trans 1,2-diols provided dicarboxylic acids through the C–C bond cleavage (entries 13–15).

Oxidation of Primary Alcohols and Aldehydes to Carboxylic Acids. In the oxidation of octyl alcohol we met with some difficulties in producing the corresponding carboxylic acid under the acidic conditions of entry 3 (Table I). As shown in entry 17 (Table III), the yield of octanoic acid could be improved to 68% yield from 45% (entry 16) when the electrolysis was conducted at pH 7. The oxidation of primary alcohols with the exception of benzyl alcohol (entry 20) usually proceeded sluggishly in low yields (60–77%) (entries 16–19, Table III) and required about 6–7 F/mol of electricity to complete the conversions. In the case of octyl alcohol which lacks substituents at the C-2 position, a small amount of dimeric ester (13–16%) was observed, formed presumably via a hemiacetal intermediate (entries 16 and 17, Table III). These results suggest that this electrooxidation appears to be slightly influenced by geometric or steric constraints (compare entries 18 and 19, Table III). Aromatic and aliphatic aldehydes were converted into the corresponding carboxylic acids smoothly (entries 21 and 22, Table III).

It was suggested by Sharpless et al.[11] that a lower valent oxoruthenium carboxylate complex may be formed accompanying the loss of catalyst activity when carboxylic acids are either present or generated in the course of oxidation with ruthenium(VIII) tetraoxide. As shown in Table IV, we examined the catalytic activity of a μ_3-oxoruthenium carboxylate complex by using $[Ru_3O(OAc)_6]^{+-}OAc$[13] toward the electrooxidation of secondary and primary alcohols to the corresponding ketone **2** and carboxylic acid, respectively. It was found that this Ru(III)/Ru(II) mixed valence complex was slightly less active when the electrolysis of the secondary alcohol **1** was carried out at pH 4. However, the same electrolysis of the primary alcohol at either pH 7 or pH 4 proceeded smoothly, in analogy with $RuO_2 \cdot 2H_2O$, giving the corresponding carboxylic acid in almost identical yields (Table IV).

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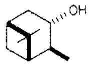
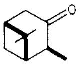
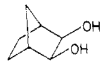
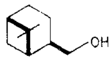
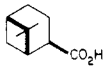
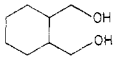
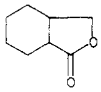
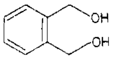
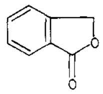
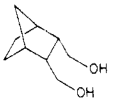
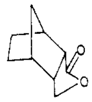
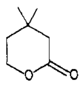
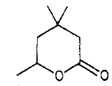
(11) Carlson, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.* **1981**, *46*, 3936.

(12) Crawford, R. J. *J. Org. Chem.* **1983**, *48*, 1366.

(13) Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1972**, 1570.

Table III. Electrooxidation of Secondary and Primary Alcohols, Aldehydes, and 1,*n*-Diols with Ruthenium Tetraoxide[a]

entry	alcohol	aqueous solution[b]	electricity, F/mol[c]	product (yield, %)[d]
1	2-octanol	A	2.4	2-octanone (90)
2	2-tetradecanol	A	2.4	2-tetradecanone (93)
3	cyclooctanol	A	2.4	cyclooctanone (88)
4	cyclododecanol	A	2.5	cyclododecanone (92)
5	*l*-menthol	A	2.4	*l*-menthone (88)
6		A	2.8	 (91)
7	2,5,5-trimethylcyclohexanol	A	2.5	2,5,5-trimethylcyclohexanone (92)
8	1-phenyl-1-propanol	A	2.4	phenethyl ketone (91)
9	diphenylcarbinol	A	2.4	benzophenone (92)
10	2-nitro-3-nonanol	A	2.7	2-nitro-3-nonanone (83)
11	1,1-dichloro-2-octanol[e]	A	2.2	1,1-dichloro-2-octanone (83)
12	cyclohexane-1,4-diol[f]	A	4.4	cyclohexane-1,4-dione (94)
13	*cis*-cyclohexane-1,2-diol[g]	B	8.8	adipic acid (75)[h]
14	*trans*-cyclohexane-1,2-diol[g]	B	6.7	adipic acid (75)[h]
15	 [g]	B	8.7	cyclopentane-1,3-dicarboxylic acid (74)[h]
16	1-octanol	A	6.2	octanoic acid (55)[h] and octyl octanoate (13)
17	1-octanol	B	6.8	octanoic acid (68)[h] and octyl octanoate (16)
18	cyclohexylmethanol	B	6.0	cyclohexanecarboxylic acid (76)[h]
19		B	7.0	 (77)[h]
20	benzyl alcohol	B	4.0	benzoic acid (90)[h]
21	benzaldehyde	B	4.0	benzoic acid (80)[h]
22	heptanal	B	4.0	heptanoic acid (86)[h]
23		B	5.8	 (79)
24		B	7.0	 (60)
25		B	8.1	 (83)
26		B	7.1	 (74)
27	decane-1,4-diol	B	6.9	decan-4-olide (79)
28		B	5.0	 (75)
29	decane-1,5-diol	B	5.7	decan-5-olide (79)
30	undecane-1,6-diol	B	10.0	6-oxoundecanoic acid (65)[h]
31	dodecane-1,7-diol	B	10.7	7-oxododecanoic acid (69)[h]
32	undecane-1,10-diol	B	8.5	10-oxoundecanoic acid (89)[h]
33	tridecane-1,12-diol	B	13.1	12-oxotridecanoic acid (85)[h]
34	hexadecane-1,15-diol	B	11.5	15-oxohexadecanoic acid (80)[h]

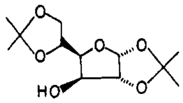
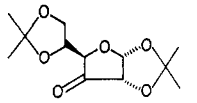
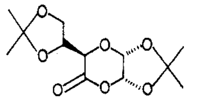
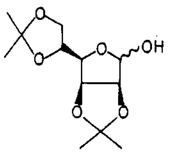
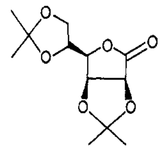
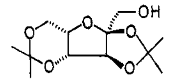
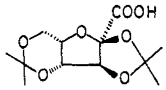
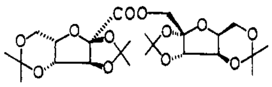
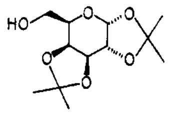
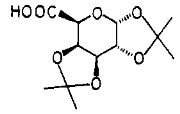
[a] Unless otherwise noted, all electrolyses were carried out using 1.0–1.5 mmol of alcohols and 0.02–0.04 mmol of $RuO_2 \cdot 2H_2O$ in CCl_4 (5 mL)–saturated NaCl (10 mL) with Pt foil electrodes (3 cm^2) under a constant current of 60 mA (applied voltage: 2–4 V) in an undivided cell. [b] Aqueous electrolyte solution: A = saturated NaCl buffered at pH 4 by 0.2 M NaH_2PO_4, B = saturated NaCl at pH 7. [c] Consumed electricity based on the substrates. [d] Based on isolated products after column chromatography (SiO_2). [e] Carried out under a constant current density of 10 mA/cm^2. [f] Carried out in saturated NaCl buffered at pH 4 without using CCl_4. [g] Carried out in saturated NaCl (pH 7) without using CCl_4. [h] Isolated as methyl ester (with CH_2N_2 in ether) and purified by column chromatography (SiO_2).

Table IV. Electrooxidation with $Ru_3O(OAc)_6(H_2O)_3{}^{+-}OAc$ as a Catalyst[a]

entry	alcohol	pH in aqueous phase	F/mol	product yield, %[b]	recovery of alcohol, %
1	4-*tert*-butyl-cyclohexanol	7	2.4	81	trace
2	4-*tert*-butylcyclohexanol	4[c]	2.4	75	16
3	cyclohexylmethanol	7	4.8	71	trace
4	cyclohexylmethanol	4[c]	4.8	72	trace

[a] Carried out using 1.0 mmol of alcohols and 5 mg (0.006 mmol) of $Ru_3O(OAc)_6(H_2O)_3{}^{+-}OAc$ in CCl_4 (5 mL)–saturated NaCl (10 mL) system under a current of 20 mA/cm^2 (applied voltage: 2.0–3.0 V) at room temperature in an undivided cell. [b] Based on isolated products. [c] Used buffer solution of 0.2 M NaH_2PO_4.

Table V. Electrooxidation of Some Carbohydrate Derivatives with Ruthenium Tetraoxide[a]

entry	alcohol	solvent system[b]	mA/cm^2 (F/mol)	product (yield, %[c])
1		B	20 (6.5)	 (88-90)
				 (3-5)
2		C	10 (3.2)	 (92)
3		A	16.7 (7.0)	 (83)
				 (1.8)
4		A	17 (6.9)	 (86)

[a] Unless otherwise noted, electrolyses were carried out using 1.0–1.5 mmol of alcohols and 0.02–0.04 mmol of $RuO_2 \cdot 2H_2O$ at room temperature in an undivided cell. [b] Solvent system in electrolysis: A = CCl_4 (5 mL)–saturated NaCl (buffered solution at pH 7, 10 mL), B = CCl_4 (3 mL)–*t*-BuOH (2 mL)–saturated NaCl (10 mL), C = acetone (5 mL)–saturated NaCl (pH 7, 10 mL). [c] Based on isolated products.

Oxidation of 1,*n*-Diols to Lactones and Keto Acids. Recently, it has been reported that $RuCl_2(Ph_3P)_4$,[14] $RuH_2(Ph_3P)_4$,[15] and $Ru_3(CO)_{12}$[16] are effective dehydration catalysts for 1,4- and 1,5-diols in the presence of adequate hydrogen acceptors to produce the corresponding γ- and δ-lactones. Furthermore, $RuCl_2(Ph_3P)_3$[17] has been exploited for selective oxidation of primary alcohols to the corresponding aldehydes and γ-lactones. However, to our knowledge there is no report on the synthesis of lactones by the oxidation of diols with ruthenium tetraoxide. As shown in entries 23–26 (Table III), the electrooxidation of bis primary 1,4- and 1,5-diols in a CCl_4-saturated NaCl (pH 7)–Pt system afforded the corresponding γ- and δ-lactones smoothly. Of particular interest is the oxidation of diols bearing a pair of primary and secondary hydroxyl groups at 1,4- and 1,5-positions to produce the corresponding γ- and δ-lactones, presumably as a result of initial oxidation of the primary hydroxyl group at the terminal position followed by the oxidation of the resulting intermediary lactol (entries 27–29). However, diols whose secondary hydroxyl groups were separated by more than four methylene linkages from the terminal hydroxyl group produced the corresponding keto acids predominantly (entries 30–34).

Oxidation of Carbohydrate Derivatives. There is continuous interest in developing a convenient procedure to oxidize carbohydrates,[18] since they are now widely used as chiral templates for the enantioselective synthesis of biologically active natural products.[19] As the extension of the present work, we examined the oxidation of some carbohydrates partially protected as acetonides. The electrooxidations were performed under an almost neutral conditions and the results are listed in Table V. In the oxidation of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose in a CCl_4 (3 mL)–*t*-BuOH (2 mL)–saturated NaCl (10 mL) system (entry 1), slight overoxidation of the ketone to the lactone was observed from the initial stage of the reaction.[20] The oxidation of the lactol (entry 2) was carried out successfully in an acetone–saturated NaCl (buffered solution of pH 7) system, instead of employing a clearly separated two-phase system of CCl_4–saturated NaCl. As shown in entry 3, 2,3:4,6-di-*O*-isopropylidene-L-sorbose was smoothly converted into keto-L-gulonic acid, an important intermediate for L-ascorbic acid (vitamin C) synthesis,[21] though the formation of a small amount of dimeric ester is accompanied. In this case, it is necessary to neutralyze the liberated acid by adding 5% sodium bicarbonate during the electrolysis. Similar electrolysis of the primary alcohol, 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, provided the corresponding galacturonic acid, in good yield (entry 4).

In conclusion, we have explored in this work the utility of the double mediatory system for the electrooxidation of alcohols and aldehydes to the carbonyl compounds and also demonstrated the efficiency of ruthenium tetraoxide as a recycling, oxidizing catalyst. Good results were obtained and may be attributed to the two-phase system in which the oxidation of the substrate and regeneration of

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oxidants were carried out separately. The simplicity of product isolation and the relatively low cost of the oxidants make this procedure a potential alternative to standard methods of oxidation which require stoichiometric amount of either metal oxidant or expensive reagents.

Experimental Section

Melting points are uncorrected and boiling points are indicated by an air-bath temperature without correction. IR spectra were recorded with a JASCO IRA-1 grating spectrometer. Unless otherwise noted, ^1H NMR spectra were determined at 60 MHz with a Hitachi R-24 spectrometer. ^{13}C NMR spectra were recorded with a JEOL FX-100 spectrometer at 25.05 MHz. Samples were dissolved in $CDCl_3$ and the chemical shifts are expressed in δ values (ppm) relative to Me_4Si as an internal standard. Optical rotations were taken on a JASCO DIP-140 digital polarimeter. Elemental analyses were performed in our laboratory.

Materials. $RuO_2{\cdot}2H_2O$, $RuCl_3{\cdot}(H_2O)_x$, and $Ru_3(CO)_{12}$ purchased from Nippon Engelhard Company were used. Commercially available starting alcohols were used as received, and other alcohols prepared by using known methods were purified by distillation or column chromatography prior to use. Carbon tetrachloride was distilled once over P_2O_5 before use, and the aqueous buffered solution was prepared by dissolving appropriate phosphate salts in aqueous sodium chloride.

Electrolysis Apparatus. Electrolyses were usually carried out in a 30 mL glass cell (2.5 cm diameter and 10 cm height) fitted with a gas lead pipe, a stirring bar, and two platinum foil electrodes (3 cm^2) placed parallel to each other 15 mm apart (Figure 1). The vessel was immersed in a water bath maintained in a range of 15–20 °C.

Generation of RuO_4 from $RuO_2{\cdot}2H_2O$ by Electrolysis. $RuO_2{\cdot}2H_2O$ (20.2 mg, 0.12 mmol) suspended in CCl_4 (5 mL)–saturated NaCl (buffered at pH 4 with 0.2M NaH_2PO_4, 10 mL) was electrolyzed at a constant current of 20 mA/cm^2 (applied voltage: 1.8 V) with a vigorous stirring. The CCl_4 layer turned pale yellow with RuO_4 when 4 F/mol of electricity (based on $RuO_2{\cdot}2H_2O$) has been passed (it took about 12.9 m). The mixture was filtered off and CCl_4 layer was separated from the filtrate and then treated with excess of 2-propanol at 0.5 °C to regenerate ruthenium dioxide. Evaporation of solvent followed by washing with CCl_4 and water left 18.4 mg (91.1%) of $RuO_2{\cdot}2H_2O$ as a black solid.

General Procedure for Electrooxidation of Secondary Alcohols. 4-*tert*-Butylcyclohexanol (1, 156 mg, 1.0 mmol) was dissolved in CCl_4 (5 mL) in a electrolysis vessel and to this solution was added $RuO_2{\cdot}2H_2O$ (3 mg, 0.02 mmol) and saturated NaCl buffered at pH 4 with 0.2 M NaH_2PO_4 (10 mL). In the upper aqueous layer of the biphase mixture was immersed two platinum foil electrodes, and the mixture was electrolyzed under a constant current of 20 mA/cm^2 by changing the current direction every 30 s with slight vigorous stirring. The electrolysis was continued until the organic phase changed to a slight yellow solution from dark black (it required the passage of about 2.4 F/mol of electricity based on the alcohol 1). The mixture was then treated with 2-propanol (0.5 mL) to destroy the excess ruthenium tetraoxide and filtered off. The CCl_4 layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined extracts were washed with water, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, hexane–AcOEt, 5:1) to give 143 mg (93%) of 4-*tert*-butylcyclohexanone (2): mp 47–49 °C; IR (Nujol) 1715 (C=O), 1580, 1370, 1220, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (s, 9, CH_3), 1.15–1.65 (m, 4, CH_2), 1.70–2.45 (m, 5, CH_2CO, CH).

Similar electrolysis of 2.34 g (15 mmol) of 1 using 6 mg (0.035 mmol) of $RuO_2{\cdot}2H_2O$ in the same electrolysis medium as above took about 2.6 F/mol of electricity to complete the conversion and the desired ketone 2 was obtained in 93% yield.

Oxidation of 1 in a Circulating Flow Cell. Procedure for a Large-Scale Operation. Into a flow cell as depicted in Figure 2 (200 mL volume) were added 4-*tert*-butylcyclohexanol (1, 18 g, 115 mmol), $RuO_2{\cdot}2H_2O$ (58 mg, 0.34 mmol), CCl_4 (60 mL), saturated NaCl (120 mL), NaH_2PO_4 (3.7 g). These substances were mixed by being circulating at a linear rate of ca. 10 cm/s by a glass-coated flowing-pump. The resulting suspension was electrolyzed at a constant current of 1.8 A with three graphite plate electrodes (59 × 29 × 5 mm) as an anode. During the electrolysis, the pH and temperature of the solution was maintained at a pH range of 3–5 and 20–25 °C, respectively. The electrolysis was continued until 3.1 F/mol of electricity has been passed. The mixture was then treated with 2-propanol and filtered to recover most of the catalysts. The organic phase was separated and the aqueous layer was extracted several times with $CHCl_3$. Combined extracts were dried over Na_2SO_4 and concentrated to give 18.75 g of the crude product which was purified by column chromatography (SiO_2, hexane–AcOEt, 9:1) to give 16.8 g (95 %: current efficiency 60.4 %) of 2 as solids.

Oxidation of Secondary Alcohols Miscible with Water. A mixture of cyclohexane-1,4-diol (128.5 mg, 1.11 mmol) and $RuO_2{\cdot}2H_2O$ (3.3 mg, 0.02 mmol) in saturated NaCl (buffered at pH 4 with 0.2 M NaH_2PO_4, 10 mL) was electrolyzed under a constant current of 20 mA/cm^2 (applied voltage: 2–4 V) at 10–15 °C. After 4.4 F/mol of electricity has been passed, the mixture was treated with 2-propanol (0.5 mL) and concentrated in vacuo. The residue was extracted with AcOEt (10 mL × 3) and the extracts were dried (Na_2SO_4). Evaporation followed by purification on column chromatography (SiO_2, hexane–AcOAt, 3:1) gave 116.8 mg (94%) of cyclohexane-1,4-dione: mp 77–78 °C; IR ($CHCl_3$) 3000, 1720 (C=O), 1418, 1118, 962 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.74 (s, 8, $COCH_2$).

Oxidation of 1,2-Diols. A mixture of *cis*-cyclohexane-1,2-diol (123.6 mg, 1.06 mmol) and $RuO_2{\cdot}2H_2O$ (3.9 mg, 0.02 mmol) in saturated NaCl (unbuffered solution, 10 mL) was electrolyzed under a constant current of 20 mA/cm^2 (applied voltage: 2–4 V). After passage of 14.4 F/mol of electricity, the reaction was quenched with 2-propanol (1 mL). Extractive workup with CH_2Cl_2 followed by esterification of the crude product with excess CH_2N_2 in ether gave 135.9 mg (73 %) of dimethyl adipate after purification on column chromatography (SiO_2, hexane–AcOEt, 3:1).

Oxidation of Primary Alcohols. A mixture of cyclohexylmethanol (133.9 mg, 1.17 mmol) and $RuO_2{\cdot}2H_2O$ (3.7 mg, 0.02 mmol) in CCl_4 (5 mL)–saturated NaCl (unbuffered solution, 10 mL) was electrolyzed in a similar manner as described for the oxidation of secondary alcohols by passing 6.0 F/mol of electricity. Extractive workup including acidification with 10% tartaric acid followed by esterification of the crude product with CH_2N_2 in ether gave 127.1 mg (76%) of methyl cyclohexanecarboxylate after purification by column chromatography (SiO_2, hexane–AcOEt, 4:1).

Oxidation of 1,*n*-Diols. Oxidation of decane-1,5-diol (193 mg, 1.1 mmol) was carried out in a CCl_4 (5 mL)–saturated NaCl (pH 7, 10 mL) system in the presence of $RuO_2{\cdot}2H_2O$ (3.4 mg, 0.02 mmol) by passing 5.7 F/mol of electricity under a constant current of 20 mA/cm^2 (applied voltage: 2–4 V). Extractive workup followed by purification of the crude product on column chromatography (SiO_2, hexane–AcOAt, 3:1) gave 150 mg (79 %) decan-5-olide: bp 121–123 °C (3 mm) (lit.[22] bp 157 °C (11 mm)); IR (neat) 1731 (lactone C=O), 1464, 1340, 1140, 1120, 1050, 1038, 938 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (m, 3, CH_3), 1.30–2.13 (m, 12, CH_2), 2.28–2.69 (m, 2, CH_2CO), 4.08–4.52 (m, 1, CHO).

Oxidation of Carbohydrate Derivatives. A solution of 2,3:4,6-di-*O*-isopropylidene-α-L-sorbofuranose (263 mg, 1.0 mmol) and $RuO_2{\cdot}2H_2O$ (3.7 mg, 0.02 mmol) in CCl_4 (5 mL)–saturated NaCl (unbuffered solution, 10 mL) was electrolyzed under a constant current of 16.7 mA/cm^2. In the course of the reaction, the mixture was neutralized by adding 0.5 mL of 4.2% $NaHCO_3$ after 2 F/mol of electricity has been passed. After passage of 8 F/mol of electricity, the mixture was made slightly alkaline (pH 8–9) with saturated $HaHCO_3$ and neutral products were removed by washing with CH_2Cl_2. The aqueous layer was acidified with 10% tartaric acid (pH 3–4) under cooling and extracted with CH_2Cl_2 (5 mL × 2). The extracts were washed with brine, dried (Na_2SO_4), and concentrated to give 231.1 mg (83%) of 2,3:4,6-di-*O*-isopropylidene-2-ketogulonic acid: mp 104–106 °C (from AcOEt) (lit.[23] mp 98–99 °C); $[\alpha]^{14}_D$ +8.2° (*c* 1.08 in H_2O); IR ($CHCl_3$) 3365 (COOH), 1780 (C=O), 1446, 1371, 1085, 1054, 965, 905, 857, 816 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$) δ 1.38, 1.46, 1.53, 1,58 (s, 12, CH_3), 3.94 (br, 1, COOH), 4.17 (m, 2, CH_2O), 4.30 (m,

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1, CHO), 4.45 (m, 1, CHO), 4.67 (s, 1, CHO). From the neutral extract portion was isolated 9.4 mg (1.8%) of dimeric ester by cautious chromatography (SiO_2, hexane–AcOEt, 2:1); IR (neat) 1748 (C=O), 1447, 1385, 1378, 1200, 1160, 1120, 1088, 1076, 987, 948, 907, 866, 830 cm^{-1}.

Physical and spectral data for selected compounds in Tables III and V are as follows. (1*S*,2*S*,5*R*)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-one: bp 127–129 °C (9 mm) (lit.[24a] bp 54–56 °C (1 mm); $[\alpha]^{23}_{\mathrm{D}}$ −15.5° (*c* 0.72 in MeOH) (lit.[24a] value of *d* enantiomer is +10.3°).

2-Nitro-3-nonanone:[25] bp 125–127 °C (9 mm); IR (neat) 1725 (C=O), 1560 (NO_2), 1450, 1402, 1380, 1050, 875 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 0.89 (m, 3, CH_3), 1.30 (m, 6, CH_2), 1.66 (m, 2, CH_2), 1.70 (d, *J* = 7 Hz, 3, $C(NO_2)CH_3$), 2.58 (t, *J* = 7 Hz, 2, $COCH_2$), 5.23 (q, *J* = 7 Hz, 1, $COCHNO_2$); ^{13}C NMR ($CDCl_3$) δ 14.0 (q), 15.0 (q), 22.5 (t), 23.2 (t), 28.5 (t), 31.5 (t), 39.1 (t), 88.9 (d), 199.8 (s). Anal. Calcd for $C_9H_{17}NO_3$: C, 57.73; H, 9.15. Found: C, 57.95; H, 9.34.

1,1-Dichloro-2-nonanone: bp 105–107 °C (9 mm); IR (neat) 1735 (C=O), 1468, 1405, 1380, 1220, 1145, 1100, 1060, 785, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (m, 3, CH_3), 1.32 (m, 8, CH_2), 2.78 (t, *J* = 6.5 Hz, 2, $COCH_2$), 5.73 (s, 1, $COCHCl_2$). Anal. Calcd for $C_8H_{14}Cl_2O$: C, 48.75; H, 7.16. Found: C, 48.63; H, 7.03.

Dimethyl *cis*-cyclopentane-1,3-dicarboxylate: bp 100–102 °C (9 mm) (lit.[26] bp 140 °C (25 mm)); ^{13}C NMR ($CDCl_3$) δ 29.1 (t, 2 C), 33.4 (t), 43.8 (d, 2 C), 51.8 (q, 2 C), 175.7 (s, 2 C).

Methyl (1*S*,2*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]heptane-2-carboxylate:[27] bp 106–108 °C (9 mm); $[\alpha]^{23}_{\mathrm{D}}$ −21.4° (*c* 1.06 in EtOH); IR (neat) 1736 (ester C=O), 1434, 1359, 1326, 1202, 1070, 1016 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.79, 1.21 (s, 6, CH_3), 1.17 (d, *J* = 9 Hz, 1, CH), 1.65–2.12 (m, 7, CH_2, CH), 2.78–3.30 (m, 1, CHO), 3.77 (s, 3, OCH_3).

1,2-*cis*-2-(Hydroxymethyl)cyclohexane-1-carboxylic acid, γ-lactone (tetrahydrophthalide): bp 133–135 °C (15 mm) (lit.[28] bp 122 °C (9–10 mm)); ^{13}C NMR ($CDCl_3$) δ 22.6 (t), 23.0 (t), 23.5 (t), 27.2 (t), 35.4 (d), 39.5 (d), 71.8 (t), 178.5 (s).

Phthalide: mp 71–72 °C (lit.[29] mp 72–73 °C).

***endo*-2,3-*cis*-3-(Hydroxymethyl)norbornane-2-carboxylic acid, γ-lactone**: mp 147–148 °C (lit.[30] mp 148–149 °C).

3,3-Dimethylpentan-5-olide: bp 140–142 °C (19 mm) (lit.[31] bp 110 °C (10 mm)); IR (neat) 1730 (lactone C=O), 1460, 1400, 1365, 1250, 1210, 1165, 1075, 1035 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 6, CH_3), 1.69 (t, *J* = 6 Hz, CH_2), 2.31 (s, 2, $COCH_2$), 4.35 (t, *J* = 6 Hz, CH_2O).

Decan-4-olide: bp 156–158 °C (18 mm) (lit.[32] bp 84 °C (0.2 mm)).

3,3-Dimethylhexan-5-olide: bp 142–144 °C (16 mm) (lit.[33] bp 122 °C (13 mm)); IR (neat) 1730 (lactone C=O), 1450, 1383, 1370, 1264, 1245, 1172, 1138, 1042, 985, 968 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.07, 1.09 (s, 6, CH_3), 1.38 (d, *J* = 6 Hz, 3, CH_3), 1.60–2.01 (m, 2, CH_2), 2.30 (m, 2, CH_2CO), 4.25–4.80 (m, 1, CHO).

Methyl 6-oxoundecanoate: bp 113–115 °C (14 mm) (lit.[34] bp 133–135 °C (19 mm)).

Methyl 7-oxododecanoate: bp 118–120 °C (14 mm) (lit.[34] bp 139–141 °C (19 mm)).

Methyl 10-oxoundecanoate: bp 124–127 °C (5 mm) (lit.[35] bp 163 °C (13.5 mm)).

Methyl 12-oxotridecanoate: mp 31–32 °C (lit.[36] mp 32.6–33.2 °C).

Methyl 15-Oxohexadecanoate: mp 47–48 °C; IR (Nujol) 1733 (ester C=O), 1708 (C=O), 1467, 1436, 1262, 1233, 1203, 1171, 880, 712 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (m, 22, CH_2), 2.11 (s, 3, $COCH_3$), 2.29 (t, 4, $COCH_2$), 3.64 (s, 3, OCH_3); ^{13}C NMR ($CDCl_3$) δ 23.9 (t), 25.0 (t), 29.2 (t, 2 C), 29.4 (t, 3 C), 29.6 (t, 4 C), 29.9 (q), 34.1 (t), 43.8 (t), 51.4 (q), 174.3 (s), 209.3 (s). Anal. Calcd for $C_{17}H_{32}O_3$: C, 71.79; H, 11.34. Found: C, 71.93; H, 11.46.

1,2:5,6-Di-*O*-isopropylidene-α-D-ribofuranos-3-ulose: mp 105–107 °C (from ether–hexane) (lit.[37] mp 108–110 °C); $[\alpha]^{12}_{\mathrm{D}}$ +39° (*c* 0.51 in H_2O) (lit.[37] +40°); IR ($CHCl_3$) 1775 (C=O), 1455, 1376, 1215, 1155, 1085, 1022, 880, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.32, 1.45 (s, 12, CH_3), 3.90–4.50 (m, 5, CH_2O, CHO), 6.09 (d, *J* = 4.5 Hz, 1, CHO).

2,3:5,6-Di-*O*-isopropylidene-D-allono-1,4-lactone: mp 122–123 °C (lit.[38a] mp 126 °C); $[\alpha]^{18}_{\mathrm{D}}$ +50° (*c* 1.52 in $CHCl_3$) (lit.[38a] +50.6°); IR (Nujol) 1780, 1768 (lactone C=O), 1378, 1198, 1118, 1078, 1035, 973, 850 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.41, 1.45 (s, 6, CH_3), 1.50 (s, 6, CH_3), 4.14 (m, 2, CH_2O), 4.42 (m, 2, CHO), 4.90 (m, 2, CHO).

1,2:3,4-Di-*O*-isopropylidene-α-D-galacturonic acid: mp 149–151 °C (lit.[39] mp 157 °C); $[\alpha]^{18}_{\mathrm{D}}$ −92° (*c* 1.11 in $CHCl_3$) (lit.[39] −84°); IR ($CHCl_3$) 3500–2500 (COOH), 1775, 1736 (COOH), 1375, 1356, 1155, 1136, 1005, 1162, 1010, 895, 836 cm^{-1}; ^{1}H NMR (100 MHz, $CDCl_3$) δ 1.36 (s, 6, CH_3), 1.46, 1.53 (s, 6, CH_3), 4.36–4.90 (m, 5, CHO, COOH), 5.70 (d, *J* = 5 Hz, 1, CHO).

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