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A Practical Method for Alcohol Oxidation with Aqueous Hydrogen Peroxide under Organic Solvent- and Halide-Free Conditions

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A catalytic system consisting of sodium tungstate and methyltrioctylammonium hydrogensulfate effects oxidation of simple secondary alcohols to ketones using 3—30% H_2O_2 without any organic solvents. The oxidation can be conducted under entirely halide-free, mildly acidic conditions. A combination of tungstic acid and an appropriate quaternary ammonium salt also effects the alcohol dehydrogenation. The organic/aqueous biphasic reaction allows easy product/catalyst separation. The turnover number, defined as mols of product per mol of catalyst, approaches 77700 (2-octanol) or 179000 (1-phenylethanol), two orders of magnitude higher than any previously reported. Ester, alkyl and *t*-butyldimethylsilyl ether, epoxy, carbonyl, *N*-alkyl carboxamide, and nitrile groups are tolerated under the reaction conditions. Secondary alcohols are preferentially oxidized over terminal olefins. Primary alkanols are oxidized directly to carboxylic acids in a moderate to high yield. Benzylic alcohols are selectively oxidized to benzaldehydes or benzoic acids under suitable conditions. This method is high-yielding, clean, safe, operationally simple, and cost-effective, and therefore suitable for practical organic synthesis. The mechanistic origin of the catalytic efficiency is discussed.

The oxidation of alcohols is one of the most frequently used synthetic reactions in laboratory[1] and chemical manufacturing.[2] It represents an important access to essential functional groups such as ketones, aldehydes, and carboxylic acids. Since the first experiment in 1820 by Davy who oxidized ethanol with air over a platinum catalyst,[3] various methods have been elaborated which achieve the desired conversions rapidly and in good yields. Examples include high valent chromium[4] and manganese compounds,[5] sophisticated organic systems like DMSO with DCC[6] or oxalyl chloride,[7] hypervalent iodine compounds,[8] *m*-CPBA or sodium hypochlorite with TEMPO,[9] and *N*-methylmorpholine *N*-oxide with a ruthenium catalyst.[10] However, these stoichiometric oxidants possess the serious disadvantage that they are expensive and/or toxic, and produce equimolar amounts of deoxygenated wastes, which make the isolation of the products often difficult. Furthermore, inevitable co-products (*not* mitigatable by-products) represent an environmental problem and must be disposed in a costly process. The problem is serious in medium- to large-scale synthesis, especially in the chemical industry which is forced to work with bulk quantities under economic and environmental pressures. A solution can only be the employment of neat and cheap oxidants, preferably under catalytic, energy-saving conditions. Obviously, air (or molecular oxygen) and hydrogen peroxide are the oxidants of choice.[11] If such catalytic methods become available, the traditional stoichiometric oxidants will be totally abundant.[3b,12]

The attempt by Davy of 180 years ago,[3a] from this point of view, appears today very progressive, although it then was merely phenomenological and he was totally unconscious about the future environmental situation. Air is obviously the cheapest oxidant and many processes for bulk chemicals rely on it, always heterogeneously catalyzed under harsh reaction conditions and in the gas phase.[2] The reaction is often nonselective and sometimes becomes technically uncontrollable, however. The utility of air oxidation therefore is very specific and narrow. The groups led by Markó[13] and Ley[14] recently reported the utilization of air or O_2 under ambient conditions, but the efficiency can still be improved for practical use in organic synthesis.[15] A general, highly selective aerobic alcohol oxidation appears now in sight, but the current system requires a large amount of potassium carbonate or special solvents or 4 Å molecular sieves with relatively expensive ruthenium compounds. Thus, no generally applicable method exists.[16—23]

Hydrogen peroxide is likewise an ideal oxidant, particularly for batchwise production of fine chemicals using nonvolatile starting materials. Its price is expected to further drop by new manufacturing processes.[24,25] The aqueous solution less concentrated than 60% is safe and available in bulk quantities.[26] It has a high oxygen content, and the co-product of its reaction is harmless water. Because of these attractive features, considerable efforts have been made to develop suitable catalytic processes for its employment in alcohol oxidation. The first example appeared in 1979, when Jacobson and co-workers[27] found that tungsten and molybdenum peroxo complexes represent a catalytic activity for oxidation of secondary alcohols by 90% H_2O_2 in methanol. Since then, numerous reports on catalytic alcohol oxidation by H_2O_2 have appeared. Trost[28] reported the use of 30% H_2O_2 and $(NH_4)_6Mo_7O_{24}$ at room temperature, but the catalyst amount was nearly stoichiometric and the reaction needed several days. Afterward, quite a number of related procedures have appeared;[29—35] however, all of them suffer from disadvantages such as the necessity of a high concentration or a large excess of H_2O_2, long reaction times, and low catalyst activity. Furthermore, most procedures require chlorohydrocarbon solvents that affect human health and environment.[36] Use of zeolites as catalysts has allowed for oxidation without a solvent,[37] although zeolites must be prepared in an arduous process and have some disadvantages like deactivation by "bleeding".[38] Most notably, Venturello found that isolated $[CH_3(n\text{-}C_8H_{17})_3N]_3PO_4[WO(O_2)_2]_4$ displays a catalytic activity for non-solvent oxidation,[33] although much room is left for improvement.

This paper presents an environmentally-conscious, efficient procedure for alcohol oxidation using 3—30% H_2O_2 suitable for practical organic synthesis.[39] Cheap, physiologically harmless sodium tungstate was used as catalyst under phase-transfer conditions.[40] No solvent is required, but if desired, toluene as a non-halogenated liquid can be employed. The organic/aqueous biphasic system allows facile catalyst/product separation.[41] The turnover number (TON) is extremely high, and a range of functional groups is tolerated under such oxidative conditions. This method is technically and economically very attractive.

Results and Discussion

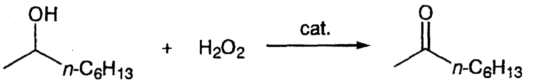
Reaction Conditions. In the search for optimum reaction conditions, oxidation of 2-octanol with 30% H_2O_2 (alcohol : H_2O_2 molar ratio = 1 : 1.2) was first examined using a 0.01 molar amount of Na_2WO_4 at 90 °C with stirring at 1000 rpm (Eq. 1). Rapid stirring is necessary to facilitate the biphasic reaction. Since the system comprises two immiscible liquid phases, the nature of the phase-transfer catalyst (PTC) is crucial. The effects of various PTCs were examined, as illustrated in Table 1. In the absence of any PTCs, 2-octanol was oxidized after 1 h in a mere 1% yield (Entry 1). $[CH_3(n\text{-}C_8H_{17})_3N]Cl$, a widely used PTC,[40] accelerated the reaction only slightly giving the ketone in 11% yield (Entry 8). Notably, the highest rate enhancement was achieved by $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ to reach 97% yield, where the initial pH value of the aqueous phase was 0.4 (Entry 2). Thus the acidic nature of PTCs is essential. A similar effect was already found in our epoxidation procedure.[42] The coexisting counter anions also affect the reactivity. The presence of a five-fold (not equimolar) amount of sodium chloride to the ammonium hydrogensulfate reduced the yield to 59% (Entry 14). In contrast, the addition of a five-fold amount of sodium sulfate did not significantly decrease the yield (95%), although $[CH_3(n\text{-}C_8H_{17})_3N]_2SO_4$ itself had only weak accelerating ability (Entries 7 and 16). Lipophilicity of the PTC is also important. Both $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ and $[(n\text{-}C_6H_{13})_3CH_3N]HSO_4$ gave good results, while $[(n\text{-}C_4H_9)_4N]HSO_4$ was only moderately active (Entries 2, 5, and 6). In addition, the molecular shape of the quaternary ammonium ions plays an important role for

Table 1. Effects of Phase-Transfer Catalysts on Oxidation of 2-Octanol[a)]

Entry	Phase-transfer catalyst	Yield[b)]/%
1	—	1
2	$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$	97
3	$[(n\text{-}C_6H_{13})_4N]HSO_4$	81
4	$[n\text{-}C_{16}H_{33}(CH_3)_3N]HSO_4$	12
5	$[(n\text{-}C_6H_{13})_3CH_3N]HSO_4$	86
6	$[(n\text{-}C_4H_9)_4N]HSO_4$	31
7	$[CH_3(n\text{-}C_8H_{17})_3N]_2SO_4$[c)]	18
8	$[CH_3(n\text{-}C_8H_{17})_3N]Cl$	11 (45[d)])
9	$[CH_3(n\text{-}C_8H_{17})_3N]Cl+H_2SO_4$ (1 : 0.5)[e)]	65
10	$[CH_3(n\text{-}C_8H_{17})_3N]Cl+H_2SO_4$ (1 : 1)[f)]	89
11	$(n\text{-}C_{16}H_{33}NC_5H_5)Cl$[g)]	7
12	$[(n\text{-}C_4H_9)_4N]Cl$	0
13	$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4+NaCl$ (1 : 1)[h)]	99
14	$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4+NaCl$ (1 : 5)[i)]	59
15	$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4+Na_2SO_4$ (1 : 1)[j)]	99
16	$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4+Na_2SO_4$ (1 : 5)[k)]	95
17	$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4+H_3PO_4$ (1 : 1)[l)]	75
18	$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4+NH_2CH_2PO_3H_2$ (1 : 1)[m)]	84

a) Reaction was run using 2-octanol, 30% H_2O_2, $Na_2WO_4\cdot 2H_2O$, and phase-transfer catalyst in a 100 : 120 : 1 : 1 molar ratio with stirring at 1000 rpm at 90 °C for 1 h. b) Determined by GC analysis. Based on 2-octanol charged. c) Molar ratio of 2-octanol, 30% H_2O_2, $Na_2WO_4\cdot 2H_2O$, and phase-transfer catalyst was 100 : 110 : 1 : 0.5. d) Reaction using a W : PTC ratio of 1 : 10 instead of standard 1 : 1. e) Reaction with a 0.005 molar amount of H_2SO_4 to 2-octanol. f) Reaction with a 0.01 molar amount of H_2SO_4 to 2-octanol. g) *N*-Hexadecylpyridinium chloride. h) Reaction with a 0.01 molar amount of NaCl to 2-octanol. i) Reaction with a 0.05 molar amount of NaCl to 2-octanol. j) Reaction with a 0.01 molar amount of Na_2SO_4 to 2-octanol. k) Reaction with a 0.05 molar amount of Na_2SO_4 to 2-octanol. l) Reaction with a 0.01 molar amount of H_3PO_4 to 2-octanol. m) Reaction with a 0.01 molar amount of $NH_2CH_2PO_3H_2$ to 2-octanol.

reactivity. Thus, [n-$C_{16}H_{33}(CH_3)_3N$]HSO_4 was much less effective than [(n-$C_6H_{13})_3CH_3N$]HSO_4 with the same atomic composition (12% vs. 86%) (Entries 4 and 5).


(1)

Tungstic acid did not catalyze oxidation of neat 2-octanol with 30% H_2O_2. However, addition of a half molar amount of [CH_3(n-$C_8H_{17})_3N$]$_2SO_4$ to the tungsten catalyst (W : ammonium = 1 : 1) gave 2-octanone in 95% yield, where the initial pH value of the aqueous phase was 0.1 (Entry 3, Table 2). Use of [CH_3(n-$C_8H_{17})_3N$]HSO_4 or [CH_3(n-$C_8H_{17})_3N$]Cl as PTC also gave the ketone in 98 and 86% yield, respectively (Entries 2 and 4). Note that these conditions were free from sodium cation. As shown in Table 2, increases in pH consistently decreased the product yield of the tungsten-catalyzed reaction. A pH value lower than 3 was necessary for the smooth biphasic oxidation. In fact, acidity of the aqueous phase was lowered as the reaction proceeded for some unknown reasons.

The catalytic activity of tungstate under homogeneous conditions was also examined with various pH values at 75 °C using 2-propanol as substrate and without PTC (Table 3). Pure tungstic acid which showed a pH value of 0.2 was reactive, while similarly high reactivity was afforded in a pH range of 0.5—2.6 as well (Entries 1—3). Sodium tungstate, giving an initial pH value of 4.6, was totally inactive (Entry 5).

In the tungsten-catalyzed reaction with a pH value below 6, unproductive decomposition of H_2O_2 is negligible. Therefore the oxidation requires only a 1.1 molar amount of H_2O_2 per alcohol to obtain a satisfactory yield. This is a logical basis of the efficiency of this method and is different from oxidation using other transition metal catalysts.[3b,12a] [CH_3(n-$C_8H_{17})_3N$]HSO_4 was found to be an optimum acidic PTC

Table 2. Effects of Cations, Anions, and pH on Oxidation of 2-Octanol[a)]

Entry	Catalyst	PTC	Additive (mol amt[b)])	pH_{init}[c)]	pH_{fin}[d)]	Yield[e)]/%
1	H_2WO_4	—	—	0.2	1.0	0
2		[CH_3(n-$C_8H_{17})_3N$]Cl	—	0.2	2.9	86
3		[CH_3(n-$C_8H_{17})_3N$]$_2SO_4$[f)]	—	0.1	2.5	95
4		[CH_3(n-$C_8H_{17})_3N$]HSO_4	—	<0	1.4	98
5		[CH_3(n-$C_8H_{17})_3N$]HSO_4	NaOH (0.5)	0.1	1.8	96
6		[CH_3(n-$C_8H_{17})_3N$]HSO_4	NaOH (1.5)	0.5	2.9	97
7		[CH_3(n-$C_8H_{17})_3N$]HSO_4	NaOH (2)	1.7	5.7	97
8		[CH_3(n-$C_8H_{17})_3N$]HSO_4	NaOH (2.5)	3.2	7.4	57
9		[CH_3(n-$C_8H_{17})_3N$]HSO_4	NaOH (3)	4.4	7.6	27
10	$Na_2WO_4\cdot 2H_2O$	—	—	4.6	7.4	1
11		[CH_3(n-$C_8H_{17})_3N$]HSO_4	H_2SO_4 (0.25)	0.1	4.9	99
12		[CH_3(n-$C_8H_{17})_3N$]HSO_4	—	0.4	4.6	96
13		[CH_3(n-$C_8H_{17})_3N$]HSO_4	NaOH (0.5)	1.6	7.0	72
14		[CH_3(n-$C_8H_{17})_3N$]HSO_4	NaOH (0.75)	3.7	7.8	54
15		[CH_3(n-$C_8H_{17})_3N$]HSO_4	NaOH (1)	4.0	7.4	27
16		[CH_3(n-$C_8H_{17})_3N$]HSO_4	NaOH (1.25)	6.4	7.9	1

a) Reaction was run using 2-octanol (20 mmol), 30% H_2O_2 (24 mmol), catalyst (0.20 mmol), PTC (0.20 mmol), and additive with stirring at 1000 rpm at 90 °C for 1 h. b) Based on catalyst. c) Initial pH value of the aqueous layer after mixing the two phases. d) Final pH value of the aqueous layer after oxidation. e) Determined by GC analysis. Based on 2-octanol charged. f) Reaction using 0.10 mmol of [CH_3(n-$C_8H_{17})_3N$]$_2SO_4$.

Table 3. Effects of Tungsten Catalysts and Initial pH on Homogeneous Oxidation of 2-Propanol[a)]

Entry	Catalyst	Additive (mol amt[b)])	pH_{init}[c)]	Convn[d)]/%
1	H_2WO_4	—	0.2	50
2		NaOH (0.5)	0.5	63
3		NaOH (1)	2.6	50
4		NaOH (2.5)	7.4	0
5	$Na_2WO_4\cdot 2H_2O$	—	4.6	0
6		H_2SO_4 (0.25)	3.3	26
7		H_2SO_4 (0.5)	1.8	61
8		H_2SO_4 (1.25)	0.7	65

a) Reaction was run using 2-propanol (20 mmol), 30% H_2O_2 (24 mmol), catalyst (0.20 mmol), and additive with stirring at 1000 rpm at 75 °C for 3 h. b) Based on catalyst. c) Initial pH value of the aqueous layer. d) Determined by GC analysis. Based on 2-propanol charged.

for oxidation of lipophilic secondary alcohols using aqueous H_2O_2 and Na_2WO_4 as catalyst. The catalytic ingredients can be reduced to a 0.002 molar amount to 2-octanol without affecting the catalytic activity. The temperature of 90 °C should be used as the optimum reaction condition. Lower temperatures decreased the yield to 57% at 60 °C and 7% at 30 °C both within 16 h. Higher temperatures are not desirable for safety reasons. Furthermore, it was noted that the rate of the 2-octanol oxidation was enhanced by the use of 3% H_2O_2 compared to 30% H_2O_2 by a factor of ca. 1.5. From a practical point of view, this may or may not be advantageous, because, on a large scale, the increased amount of water promotes transportation and heatup energy cost.

Although reaction conditions are thus variable, we choose a combined catalyst system consisting of equimolar amounts of Na_2WO_4 and $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ that dehydrogenates secondary alcohols under mildly acidic conditions. Here pH of the aqueous phase varied from 0.4 (initial) to 4.6 (final) during the reaction. Oxidation can be performed under more acidic conditions, if necessary.

Hectogram Scale Reaction. With the optimized reaction conditions in hand, a 100-g amount of 2-octanol was employed to confirm the practicability of a medium- to large-scale procedure. The alcohol (100 g) was mixed with 30% H_2O_2 (96 g), Na_2WO_4 dihydrate (0.5 g), and $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ (0.7 g) (500 : 550 : 1 : 1 mol ratio), and stirred at 90 °C at 1000 rpm. The organic layer was separated, washed with saturated $Na_2S_2O_3$ solution, and distilled to yield 95% of pure 2-octanone (93.9 g). To test the activity of recovered catalyst, the aqueous phase was utilized for reiterated oxidation. The second 100-g scale oxidation of 2-octanol with new 30% H_2O_2, combined with the distillation residue and renewed PTC, gave 2-octanone in 86% yield after distillation. In a like manner, the third run gave the ketone in 92% yield. No technical problems are seen in this reaction.

Catalytic Performance. As shown in Table 4, the catalytic efficiency of this method compares well with those of the best existing procedures. The TON, defined as mols of product per mol of catalyst, reached up to 77000 per W atom in 40% yield in the oxidation of 2-octanol with alcohol : 30% H_2O_2 : W : PTC = 200000 : 300000 : 1 : 100 (Entry 10). This TON is two orders in magnitude higher than any previously reported hydrogen peroxide oxidation. For comparison, Venturello[33] achieved a TON of 48.3/W in 96% yield with non-solvent oxidation of 2-hexanol using 40% H_2O_2 and isolated $[CH_3(n\text{-}C_8H_{17})_3N]_3PO_4[WO(O_2)_2]_4$ (Entry 6). Griffith[34] reached 130/W with 18% yield in a similar system using $[(n\text{-}C_6H_{13})_4N]_3PO_4[WO(O_2)_2]_4$ in benzene (Entry 7), while Neumann[35] reported the value of 193/W in 1,2-dichloroethane (Entry 8), the previous best record for tungsten-catalyzed reaction. Sasson achieved a TON of 513/Ru in dichloromethane but with a large excess of the oxidant due to the hydrogen peroxide-dismutating property of the Ru catalyst (Entry 3).[30] The TON value approached up to 179000 with 45% yield, when oxidation was performed with a 1-phenylethanol : 30% H_2O_2 : W : PTC ratio of 400000 : 400000 : 1 : 200 (Entry 11).

Reaction Mechanism. Although the oxidative species generated from tungstate and H_2O_2 under this catalytic condition is yet to be elucidated, it could be a bisperoxotungstate ion, $[WO(O_2)_2(OH)(H_2O)]^-$.[43]

$$Na_2WO_4 + H_2O_2 \xrightarrow{H_2O} Na_2[WO(O_2)_2(OH)_2]$$

We propose a possible catalytic cycle given in Fig. 1 (Q^+ = quaternary ammonium ion) for the biphasic oxidation. Although the reaction utilizes disodium tungstate as precatalyst,

Table 4. Comparison of Activity of Catalyst Systems in Oxidation of Secondary Alcohols with Aqueous Hydrogen Peroxide

				TON[a)] (Yield/%)		
Entry	Catalyst (mol amt)	H_2O_2/%	Solvent	2-Octanol	1-Phenylethanol	Ref.
1	$H[WO(O_2)_2(C_5H_4NCO_2)]\cdot H_2O$ (0.03)	90	CH_3OH	21 (63)	4 (96)	Jacobson[27]
2	$Na_2WO_4\cdot 2H_2O$ (0.1), $[CH_3(n\text{-}C_8H_{17})_3N]Cl$ (0.2)	70	$ClCH_2CH_2Cl$	10 (97)		Bortolini[29a]
3	$RuCl_3\cdot 3H_2O$ (0.0016),[b)] $[(CH_3)_2(n\text{-}C_{10}H_{21})_2N]Br$ (0.02)	30	CH_2Cl_2	513 (82)	561 (90)	Sasson[30]
4	$(n\text{-}C_{16}H_{33}NC_5H_5)_3(PW_{12}O_{40})$ (0.02)	35	$t\text{-}C_4H_9OH$	4 (90)	4 (96)	Ishii[31]
5	$[(dppe)Pt(CF_3)(CH_2Cl_2)]ClO_4$ (0.01)	30	$ClCH_2CH_2Cl$	33 (33)[c)]		Strukul[32]
6	$[CH_3(n\text{-}C_8H_{17})_3N]_3PO_4[WO(O_2)_2]_4$ (0.005)	40	—	48 (96)	46 (91)	Venturello[33]
7	$[(n\text{-}C_6H_{13})_4N]_3PO_4[WO(O_2)_2]_4$ (0.00035)	15	Benzene	130 (18)[d)]		Griffith[34]
8	$Na_{12}WZnMn_2(ZnW_9O_{34})_2$ (0.0002), $[CH_3(n\text{-}C_8H_{17})_3N]Cl$ (0.005)	30	$ClCH_2CH_2Cl$	193 (93)	<208 (99)	Neumann[35]
9	$Na_2WO_4\cdot 2H_2O$ (0.001), $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ (0.001)	30	—	830 (83)		This work
10	$Na_2WO_4\cdot 2H_2O$ (0.00000507), $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ (0.001)	30	—	77700 (40)		This work
11	$Na_2WO_4\cdot 2H_2O$ (0.0000025), $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ (0.0005)	30	—		179000 (45)	This work

a) Turnover number defined as mol product per mol transition metal atom of the catalyst. b) Reaction with a 2.7 molar amount of H_2O_2.
c) Oxidation of 2-hexanol. d) Oxidation of cyclohexanol.

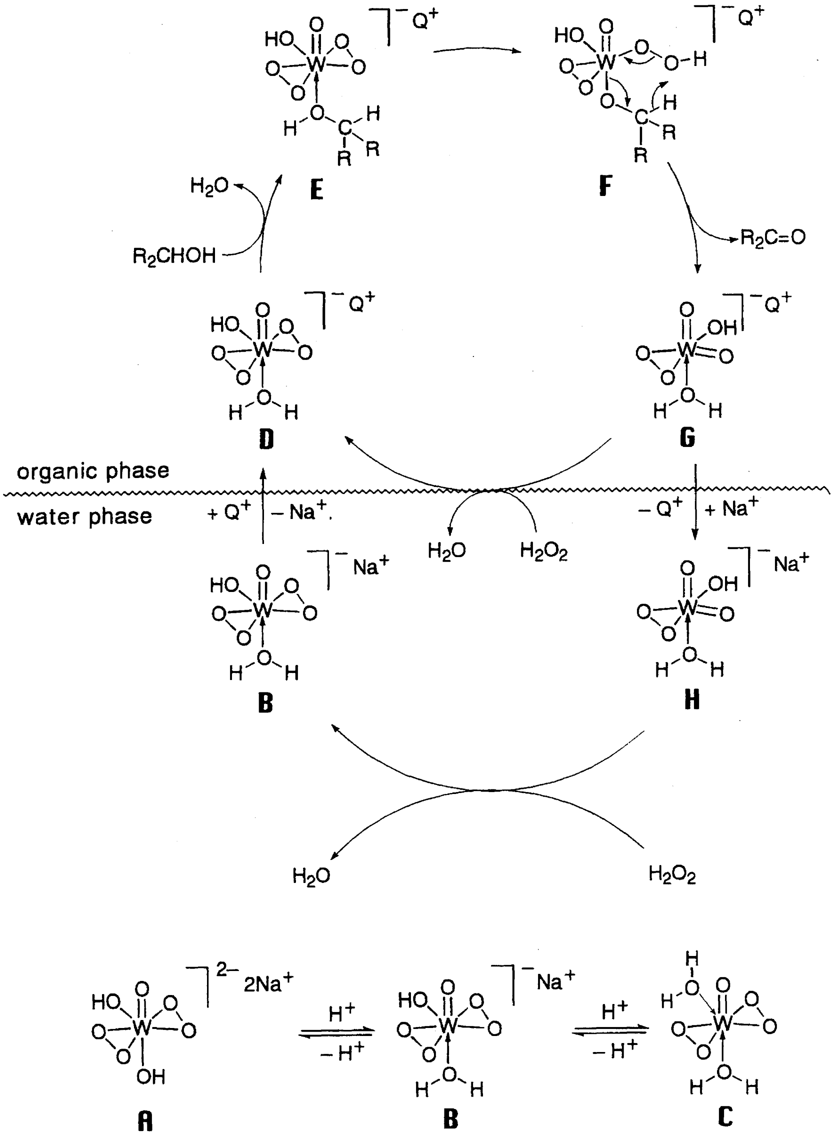


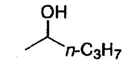
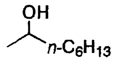
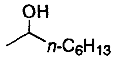
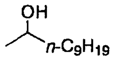
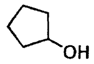
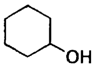
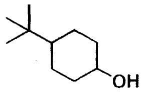
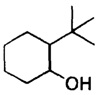
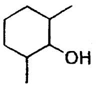
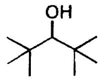
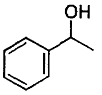
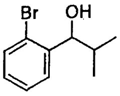
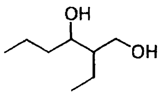
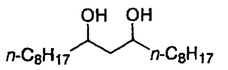
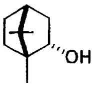
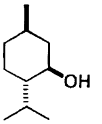
Fig. 1. Proposed catalytic cycle. Q^+ = quaternary ammonium ion.

it is readily oxidized by aqueous H_2O_2 to form an equilibrium mixture of **A**, **B**, and **C**. Since the pK_a value of **C** is known to be 0.1,[43] **B** is a dominant species under the reaction conditions with a pH range of 0.4—3. Then hydrogensulfate ions are largely deprotonated to be sulfate ions. The tungstate species **B** exists mostly as a monomer under such dilute conditions.[43,44] The results in Tables 2 and 3 suggest that this major component has enough oxidative activity toward alcohols, but that the dianion in **A** is feebly active. The minor component **C** could be reactive in homogeneous solution but is unable to move into an organic phase under the biphasic conditions. On the other hand, the anion moiety in **B** can easily be transferred to an organic phase by Na^+/Q^+ ion exchange. Thus, in the organic layer, the bisperoxo complex **D** undergoes water/alcohol ligand exchange to form **E**. Then proton transfer in **E** generates the reactive species **F**, which forms a ketonic product and **G**. The alkoxido ligand in **F** is dehydrogenated by the hydroperoxo ligand via a six-membered transition state where the hydridic α-hydrogen migrates to the positively polarized oxygen atom. This view is supported by the relative reactivity of *p*-substituted benzyl alcohols showing a ρ value of -0.31 (vide infra). The monoperoxotungstate ion in **G** is reoxidized by H_2O_2 after returning to aqueous phase as the ion pair **H**. Because the Na^+-free system using H_2WO_4 and a PTC also effects the alcohol dehydrogenation (Table 2), this step may occur at an organic/aqueous interface to some extent. In addition, oxidation of **G** could take place even in the organic phase, because 1 g of 2-octanol dissolves 0.5 mmol of H_2O_2 under the reaction conditions.

The overall reactivity is determined by the concentration of bisperoxotungstate ion and the ease with aqueous/organic phase transfer. Since the tungstate ion is hydrophilic whatever the counter cation, either Na^+ or H^+, it must interact with lipophilic Q^+ to achieve its phase transfer. Since Q^+ tends to stay in the organic layer by forming an ion pair, coexisting anions such as $SO_4{}^{2-}$, $HSO_4{}^-$, or, particularly Cl^- (Table 1), prevent effective formation of **D** which delivers the bisperoxotungstate ion from aqueous to organic phase. This undesired effect may be mitigated by using dilute aqueous H_2O_2. The marked effects of acidity and PTC on the efficiency of the 2-octanol oxidation are fully consistent with this mechanism.

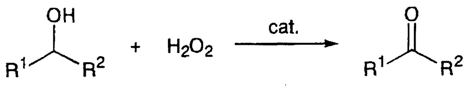
Scope of Oxidation of Secondary Alcohols. Table 5

Table 5. Oxidation of Secondary Alcohols with Aqueous Hydrogen Peroxide[a)]

	Alcohol		H_2O_2	Na_2WO_4 and PTC	Time	Ketone
Entry	Structure	mmol	mmol (equiv)	mmol (S/C)[b)]	h	Yield[c)]/%
1		1134	1247 (1.1)	2.3 (500)	4	77
2		768	845 (1.1)	1.5 (500)	4	95
3		768	845 (1.1)[d)]	1.5 (500)	4	95
4		580	638 (1.1)	1.2 (500)	4	92
5		1161	1279 (1.1)	2.3 (500)	16	70
6		998	1100 (1.1)	2.0 (500)	4	71
7		640[e)]	704 (1.1)	1.3 (500)	4	96[f)]
8		20[g)]	24 (1.2)	0.04 (500)	4	78[h)]
9		20[g)]	24 (1.2)	0.04 (500)	4	84[h)]
10		456	919 (2.0)[d)]	0.9 (500)	4	89
11		819	901 (1.1)	1.6 (500)	1	96
12		2.8	4.1 (1.5)[i)]	0.014 (200)	4	94[h)]
13		684[g)]	752 (1.1)	1.4 (500)	4	83[j)]
14		2.0[g)]	6.0 (3.0)[i)]	0.040 (50)	4	73[h,k,l)]
15		648	713 (1.1)	1.3 (500)	4	84[f)]
16		640	704 (1.1)	1.3 (500)	4	93[m)]

a) Unless otherwise stated, reaction was run with 30% H_2O_2 with stirring at 1000 rpm at 90 °C. PTC = $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$. b) Substrate/catalysts molar ratio. c) Isolated by distillation. d) Reaction with 3% H_2O_2. e) A 1 : 1 mixture of the *cis* and *trans* isomer. f) Toluene (100 mL) was used as solvent. g) A mixture of stereoisomers. h) Isolated by silica-gel column chromatography. i) Reaction with 5% H_2O_2. j) 2-Ethyl-1-hydroxy-3-hexanone. k) Toluene (1 mL) was used as solvent. l) 11-Hydroxy-9-nonadecanone. m) 99.3% stereochemically pure.

shows the oxidation of various secondary alcohols. Many of them were performed on a 100-g scale. Simple secondary alcohols were smoothly oxidized to ketones in high yield (Eq. 2).



(2)

The influence of steric factors on reactivity was tested. First, *cis*- and *trans*-4-*t*-butylcyclohexanol were found to be oxidized at equal rates, while chromic acid is known to oxidize the *cis* isomer more facilily by a factor of 3.[45] Oxidation of a mixture of *cis*- and *trans*-2-*t*-butylcyclohexanol under the standard conditions gave the cyclohexanone in a relatively high yield, 78% (Entry 8). Cyclohexanol and 2,6-dimethylcyclohexanol (a stereoisomeric mixture) were dehydrogenated at similar rates. This is contrasted to the tungsten- or molybdenum-catalyzed reaction which oxidizes the 2,6-dimethyl compound much faster.[28,33] Oxidation of sterically more hindered 2,2,4,4-tetramethylpentan-3-ol was incomplete under the usual conditions but gave di-*t*-butyl ketone in 89% yield by using two equivalents of 3% H_2O_2 (Entry 10). Oxidation of 1-(*o*-bromophenyl)-2-methyl-1-propanol using 0.005 molar amounts of the W catalyst and PTC gave *o*-bromoisobutyrophenone in 94% yield (Entry 12). Overall, the retardation by steric hindrance is not significant from a synthetic point of view.

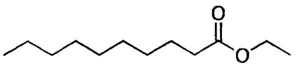
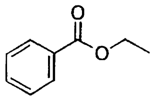
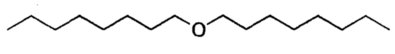
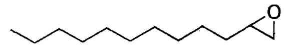
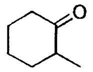
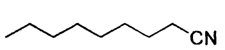
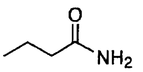
Cyclopentanol was oxidized 1.5 (competitive experiment) or 2.2 times (independent experiment) more slowly than cyclohexanol.[29b,33] This is contrary to the expectation from the higher preference of sp^2 hybridization in five-membered carbocycles.[46] Oxidation of cyclobutanol gave γ-butyrolactone as major product. The latter is derived by acid-catalyzed Baeyer–Villiger oxidation of intermediary cyclobutanone, as confirmed by a separate experiment.

The oxidation of 2-ethylhexane-1,3-diol gave selectively 2-ethyl-1-hydroxy-3-hexanone in 83% yield (Entry 13). The second oxidation was slow because it is on the less reactive primary alcohol and also due to the presence of an electron-withdrawing carbonyl group. 9,11-Nonadecanediol, a 1,3-diol, gave the corresponding β-hydroxy ketone in 73% yield (Entry 14).

In connection with terpene synthesis, (±)-isoborneol was oxidized to (±)-camphor in 84% yield, and (−)-menthol to (−)-menthone in 93% yield (Entries 15 and 16).

Chemoselectivity. In synthetic chemistry, reliable stoichiometric processes can be replaced by the catalytic counterparts only if the latter achieve the desired transformation without side reactions. A further exploration of this oxidation method revealed that the catalyst is compatible with substrates containing various functional groups. Assuming that the alcohol dehydrogenation involves ligation of the hydroxy group to the tungsten center as a necessary step (Fig. 1), we tested the oxidation of 2-octanol in toluene in the presence of an equimolar amount of a coordinative compound. As shown in Table 6, in most cases, 2-octanone was obtained without problems in >85% yield, and the additives were recovered in >95% yield. However, the reaction was significantly retarded by the presence of butyramide (Entry 7). The amide might occupy the tungsten vacant site so as to prohibit necessary alcohol coordination.

Table 6. Catalytic Activity in 2-Octanol Oxidation in the Presence of Functionalized Compounds[a)]

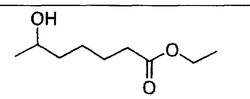
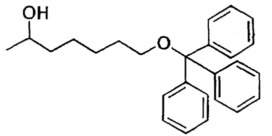
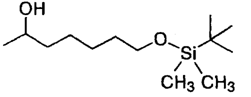
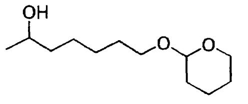
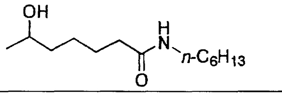
	Functionalized compound		2-Octanone
Entry	Structure	Convn[b)]/%	Yield[b)]/%
1		0	96
2		0	99
3		0	85
4		5	92
5		4	97
6		1	94
7		—	18

a) Unless otherwise stated, reaction was run using 2-octanol (10 mmol), substrate (10 mmol), 30% H_2O_2 (15 mmol), $Na_2WO_4 \cdot 2H_2O$ (0.10 mmol), $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ (0.10 mmol), and toluene (3 mL) with stirring at 1000 rpm at 90 °C for 3 h. b) Determined by GC analysis.

Along the same line, a variety of functionalized secondary alcohols were subjected to the oxidation conditions. Table 7 lists some examples. As expected, a hydroxy ester was converted to an oxo ester in a high yield (Entry 1). A trityl and *t*-butyldimethylsilyl ether were mostly tolerated under such acidic oxidation conditions (Entries 2 and 3). These protective groups may be used for selective oxidation of certain polyols. THP group can not be used for protection of primary alcohols (Entry 4). Interestingly, a hydroxy carboxamide with an *N*-alkyl group was cleanly oxidized to an oxo amide (Entry 5) (cf. Table 6). As described later, electron-rich alkoxyaromatic groups tolerate under the catalytic conditions.

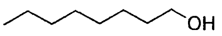
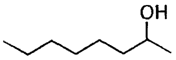
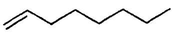
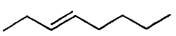
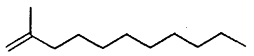
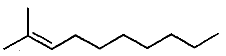
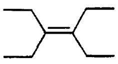
The alcohol/olefin chemoselectivity is a major concern in organic synthesis. The biphasic catalytic system is excellent for epoxidation, if (aminomethyl)phosphonic acid is added as a reaction promoter.[42] Without this additive, however, the selectivity for alcohol oxidation is significantly increased. In the absence of (aminomethyl)phosphonic acid, the rate of epoxidation is significantly lowered, while the reactivity for alcohol oxidation is not much affected. Thus the relative reactivities of 2-octanol and 1-octene in the presence and absence of (aminomethyl)phosphonic acid are 4 : 1 and 28 : 1, respectively. Table 8 compares the relative initial rates of oxi-

Table 7. Oxidation of Functionalized Secondary Alcohols[a)]

Entry	Alcohol	H_2O_2 mmol (equiv)	Time h	Convn[b)] %	Ketone Yield[b)]/%
1		12 (1.2)	4	91	87
2		12 (1.2)	4	93	92
3		12 (1.2)	4	83	77
4		15 (1.5)	2	96	12
5		12 (1.2)	4	100	95

a) Unless otherwise stated, reaction was run with alcohol (10 mmol), 5% H_2O_2 (12 or 15 mmol), $Na_2WO_4{\cdot}2H_2O$ (0.10 mmol), $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ (0.10 mmol), and toluene (2 mL) with stirring at 1000 rpm at 90 °C. b) Conversion and yield were determined by isolation using column chromatography.

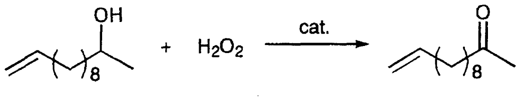
Table 8. Relative Initial Rates of Oxidation[a)]

Entry	Substrate	Relative rate[b)]
1		0.37[c)]
2		1[c)]
3		0.036
4		0.10
5		0.15
6		0.094
7		0.13
8		0.11

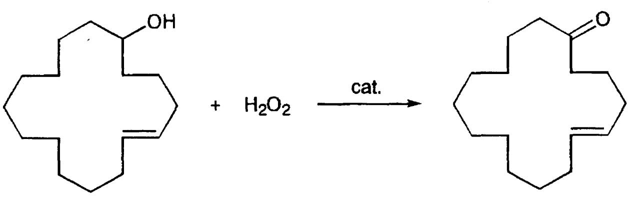
a) Reaction was run using 1- octene, olefin, 5% H_2O_2, $Na_2WO_4{\cdot}2H_2O$, and $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ in a 50 : 50 : 100 : 0.2 : 0.2 molar ratio with stirring at 1000 rpm at 110 °C in toluene (2 mL). b) Determined by GC analysis. Conversion was < 10%. c) Reaction was run using (*Z*)-3-octene and alcohol.

dation of various alcoholic and olefinic substrates. Oxidation of 2-octanol now occurs seven times faster than (*Z*)-3-octene (Entries 2 and 5), a substrate three-fold more reactive than 2-octanol in the presence of (aminomethyl)phosphonic acid.

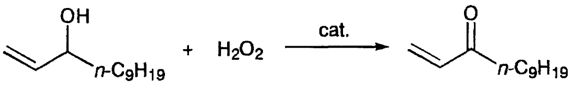
Oxidation of 11-dodecen-2-ol, a model compound containing both hydroxy and olefinic functional groups, gave 11-dodecen-2-one in 97% yield together with only 0.4% of 11,12-epoxydodecan-2-one (Eq. 3). The use of diluted H_2O_2 could shift the selectivity further toward alcohol oxidation, if very reactive double bonds are encountered. For instance, oxidation of 5-cyclohexadecenol ($E:Z=2:1$) in toluene with 5% H_2O_2 afforded 5-cyclohexadecenone in 99% yield and 100% conversion, while reaction with 30% H_2O_2 under the same conditions gave the ketone and epoxy ketone in 78 and 3% yields, respectively (86% conversion) (Eq. 4).



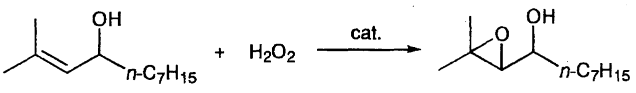
(3)



(4)



(5)



(6)

Since allylic alcohols are highly susceptible to epoxidation, their selective dehydrogenation to enones was only partially successful.[1,47,48] Oxidation of 1-dodecen-3-ol, an allylic alcohol with a terminal double bond, was converted to the desired 1-dodecen-3-one in 80% yield, contaminated with 1,2-epoxydodecan-3-ol and 1,2-epoxydodecan-3-one in 14 and 4% yields, respectively (Eq. 5). However, 2-methyl-2-undecen-4-ol with a trisubstituted olefinic bond underwent selective epoxidation in 100% yield (Eq. 6).

Oxidation of Primary Alcohols to Aldehydes and Carboxylic Acids. An important object of examinations was primary alcohols. Despite extensive studies on this subject, selective oxidation of primary alcohols to aldehydes or carboxylic acids, particularly on a preparative scale, is difficult.[1] In certain cases, oxidative degradation of products following less obvious reaction paths causes further complication. The hydrogen peroxide oxidation catalyzed by the tungsten catalyst is also not straightforward. The overall possibility is illustrated in Fig. 2. In this oxidation, water, H_2O_2, alcohols, and other nucleophiles present in the reaction system may react with the resulting aldehydes. The stability and reactivity of the tetrahedral intermediates are significantly affected by the nature of the substrates and reaction parameters, whereas most of the steps are facilitated under acidic conditions. Careful scrutiny of the nature of the reaction leads to selective oxidation of primary alcohols.

Under the present reaction conditions, 1-octanol is only 2.7 times less reactive than 2-octanol (Table 8). Certain primary alkanols are directly oxidized to carboxylic acids, if more than two molar amounts of H_2O_2 and slightly more catalyst (substrate : H_2O_2 : W : PTC = 50 : 125 : 1 : 1) are employed (Eq. 7). Table 9 lists some examples. When 100 g of 1-octanol was oxidized with 218 g of 30% H_2O_2 in the presence of 5 g of Na_2WO_4 dihydrate and 7 g of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ as PTC at 90 °C for 4 h with stirring at 1000 rpm, 96.5 g of octanoic acid (87% yield) was obtained after distillation (Entry 1). Octyl octanoate, a dimeric ester frequently obtainable via a hemiacetal (Fig. 2),[49,50] was formed in only 2% yield. Reaction with an alcohol : W ratio of 20000 : 1 led to a TON of 3000 (15% yield), which is much higher than the 363 TON value obtainable with a Ru-based catalyst in dichloromethane.[30] The reaction could not be halted at the stage of an aldehyde satisfactorily because of the rapid aldehyde oxidation that occurs via the hydrate and peroxy hydrate (Fig. 2). In fact, reaction of octanal with aldehyde : 30% H_2O_2 : W : PTC = 200 : 300 : 1 : 1 at 90 °C for 2 h afforded octanoic acid in 83% isolated yield. Even in the absence of the tungsten catalyst (aldehyde : 30% H_2O_2 : PTC = 200 : 300 : 1), octanal was converted to the carboxylic acid in 81% isolated yield.

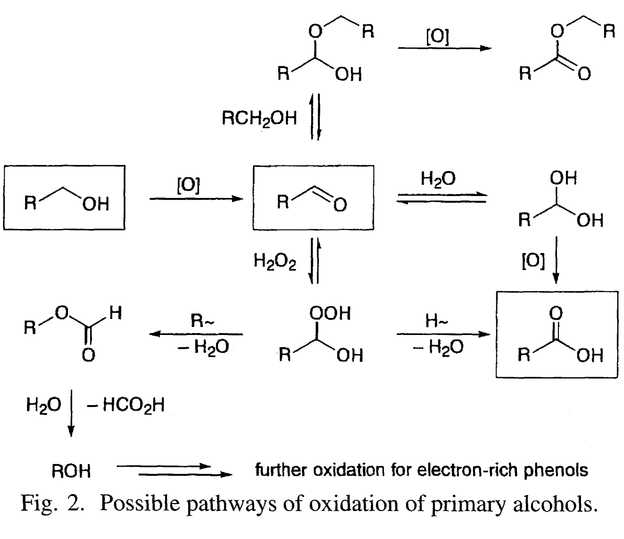
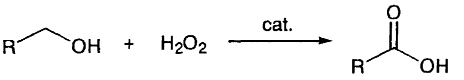


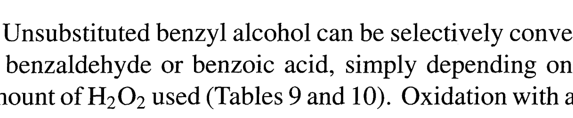
Fig. 2. Possible pathways of oxidation of primary alcohols.



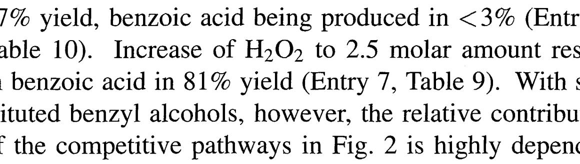
(7)

β-Branched alkanols were oxidized to carboxylic acids in a fair yield. Thus 2-ethyl-1-hexanol and neopentyl alcohol gave the corresponding acids in 68 and 52% yield, respectively (Entries 3 and 4, Table 9). The decrease in yield is due probably to the operation of the Baeyer–Villiger oxidation of intermediary aldehydes with H_2O_2. In going from straight-chain to *β*-branched alkanols, the extent of alkyl migration in the peroxy hydrate intermediate is enhanced relative to the desired hydride migration (Fig. 2).

Reactivity of *p*-substituted benzyl alcohols is dependent on the electronic properties of the substituents. Competitive experiments using a 1 : 1 mixture of benzyl alcohol and its derivative in toluene and 5% H_2O_2 in the presence of Na_2WO_4 dihydrate and $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ at 50 °C (conversion to < 10%) revealed a clean linear Hammett plot with a negative ρ value, −0.31 (Fig. 3). A similar substituent effect, $\rho = -0.27$, has been observed with stoichiometric oxidation of benzyl alcohols by a bisperoxomolybdate ion.[51,52]



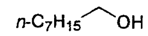
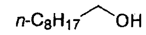
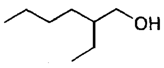
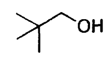
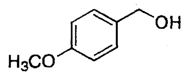
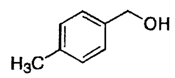
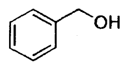
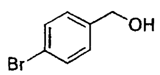
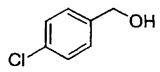
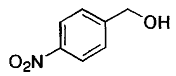
(8)



(9)

Unsubstituted benzyl alcohol can be selectively converted to benzaldehyde or benzoic acid, simply depending on the amount of H_2O_2 used (Tables 9 and 10). Oxidation with a 1.1 molar amount of H_2O_2 produces selectively benzaldehyde in 87% yield, benzoic acid being produced in < 3% (Entry 4, Table 10). Increase of H_2O_2 to 2.5 molar amount results in benzoic acid in 81% yield (Entry 7, Table 9). With substituted benzyl alcohols, however, the relative contribution of the competitive pathways in Fig. 2 is highly dependent on the electronic properties of the substituents. By selecting suitable reaction parameters, various benzylic alcohols were oxidized on a 100-g scale to the corresponding benzaldehydes in a good yield (Eq. 8).[53] Examples are given in Table 10. Satisfactory results were obtained by using < 1.5 molar amount of H_2O_2 and an alcohol : catalyst ratio of 50—330 : 1. This procedure utilized a tungsten catalyst which had been activated by a 0.1 molar amount of 5% H_2O_2. Then 30% H_2O_2 was added dropwise to a mixture of the catalyst

Table 9. Oxidation of Primary Alcohols to Carboxylic Acids[a)]

	Alcohol		H_2O_2	Na_2WO_4 and PTC	Time	Carboxylic acid
Entry	Structure	mmol	mmol (equiv)	mmol (S/C)[b)]	h	Yield[c)]/%
1		768	1920 (2.5)	15 (50)	4	87
2		693	1733 (2.5)	14 (50)	4	83
3		768	1920 (2.5)	15 (50)	4	68
4		1130	2835 (2.5)	23 (50)	4	52
5		30	150 (5)	0.30 (100)	12	5[d,e)]
6		819	4092 (5)	8.2 (100)	12	80[d,f)]
7		925	2313 (2.5)	9.3 (100)	5	81[d,f)]
8		535	2138 (4)	5.4 (100)	4	86[f)]
9		701	2806 (4)	7.0 (100)	4	87[f)]
10		653	2612 (4)	6.5 (100)	4	91[f,g)]

a) Unless otherwise stated, reaction was run with 30% H_2O_2 with stirring at 1000 rpm at 90 °C. PTC = $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$. b) Substrate/catalysts molar ratio. c) Isolated by distillation. d) A 0.1 molar ratio of 5% H_2O_2 to an alcohol was used for activation of the W catalyst, and 30% H_2O_2 was added dropwise to a mixture of the catalysts and an alcoholic substrate. e) Reaction was run in 6 mL of toluene at 70 °C. Isolated by column chromatography. *p*-Methoxybenzaldehyde was formed in 29% yield. f) Isolated by recrystallization from a 4 : 1 methanol–water mixture. g) Yield determined by HPLC was 97%.

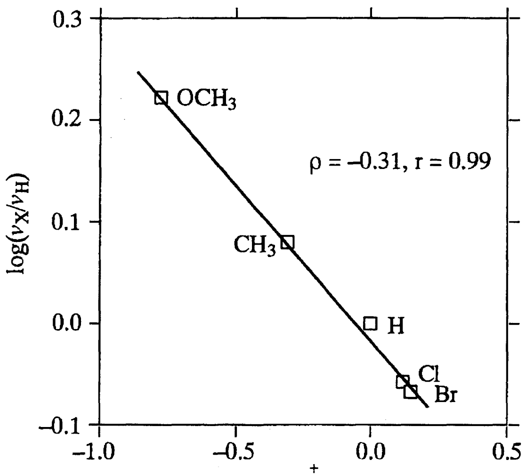
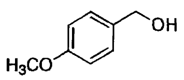
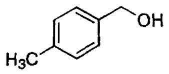
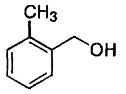
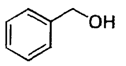
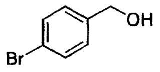
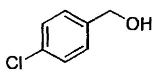
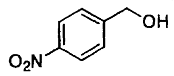
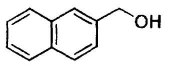


Fig. 3. Hammett plot for oxidation of *p*-substituted benzyl alcohols, *p*-$XC_6H_4CH_2OH$.

and an alcoholic substrate with stirring at 1000 rpm at 90 °C. The high efficiency of the procedure is consistent with the finding that 3—5% H_2O_2 oxidizes alcohols more rapidly than 30% H_2O_2 does. The oxidation of an oily or low-melting alcohol was accomplished without any organic solvent. Toluene could be used as solvent, if necessary. For example, the oxidation of aldehydes such as *p*-methoxybenzyl alcohol which have low log *P* values[54] was better conducted in toluene. This catalyst system is more reactive than Venturello's $[CH_3(n\text{-}C_8H_{17})_3N]_3PO_4[W(O)(O_2)_2]_4$ which was used for solvent-free oxidation of benzyl alcohol and its *p*-methyl derivative.[33] In addition, unlike oxidation with quaternary ammonium chlorides as PTC[29a] that requires 70% H_2O_2 and 1,2-dichloroethane as solvent, this reaction is achievable under milder conditions. Thus even *p*-methoxybenzyl alcohol, considered as the most difficult substrate,[33] gave the aldehyde in 90% yield (Entry 1). However, oxidation of *p*-nitrobenzyl alcohol is still difficult; the highest yield obtained so far is 59% (Entry 7).

A range of benzyl alcohols was directly oxidized to the corresponding benzoic acid derivatives using a 2.5—5 molar amount of H_2O_2 (2 molar amount in theory) and a 0.01 molar amount of Na_2WO_4 and the PTC (Eq. 9). Table 9 lists some

Table 10. Oxidation of Benzylic Alcohols to Benzaldehydes[a)]

	Alcohol		H_2O_2	Na_2WO_4 and PTC	Time	Aldehyde
Entry	Structure	mmol	mmol (equiv)	mmol (S/C)[b)]	h	Yield[c)]/%
1		724	1086 (1.5)	14.5 (50)	5	90[d,e)]
2		819	983 (1.2)	4.1 (200)	4.5	91
3		819	983 (1.2)	4.1 (200)	4.5	88
4		925	1018 (1.1)	2.8 (330)	3	87
5		535	696 (1.3)	2.7 (200)	4.5	81
6		701	841 (1.2)	3.5 (200)	4.5	82
7		5	10 (2)	0.1 (50) 0.05 (100)	17	59[f,g,h)]
8		632	759 (1.2)	3.2 (200)	4.5	82[i)]

a) Unless otherwise stated, a 0.1 molar ratio of 5% H_2O_2 to an alcohol was used for activation of the W catalyst, and 30% H_2O_2 was added dropwise to a mixture of the catalysts and an alcoholic substrate with stirring at 1000 rpm at 90 °C. PTC = $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$. b) Substrate/catalysts molar ratio. c) Isolated by distillation. d) Toluene (150 mL) was used as solvent. e) Reaction at 70 °C. f) Determined by HPLC analysis. g) Toluene (8 mL) and ethyl acetate (2 mL) were used as solvent. h) Conversion was 80%. i) Reaction was run using 5% H_2O_2 with stirring at 1000 rpm at 90 °C.

examples. Separate experiments using 30% H_2O_2 with or without the tungsten catalyst revealed that the benzoic acids are derived from the benzaldehyde intermediates via dual pathways, viz., the tungsten-catalyzed dehydrogenation of aldehyde hydrates (minor) and the acid- catalyzed Baeyer–Villiger reaction via aldehyde peroxy hydrates (major), as illustrated in Fig. 2. Peroxybenzoic acids might also participate, but only to a little extent. Thus reaction of benzaldehyde and 30% H_2O_2 in the presence of the tungsten catalyst and PTC (100 : 250 : 1 : 1 mol ratio) at 90 °C for 3 h gave benzoic acid in 91% yield. In the absence of the tungsten catalyst, the acid was obtained in 85% yield under otherwise identical conditions. The latter was not a pure "back-ground" reaction, because the acidity of the reaction system was significantly increased by the removal of the tungsten salt. However, the operation of the dual pathways is obvious. The extent of the Baeyer–Villiger route relative to dehydrogenation of aldehyde hydrates increases with electron-withdrawing substituents. In any case, the peroxy hydrates are transformed to either the desired benzoic acids via hydride migration or to aryl formates via aryl migration by a Baeyer–Villiger mechanism. The latter undesired pathway becomes significant with electron-donating substituents, since the resulting phenols are further oxidized to give complex mixtures. Therefore, *p*-methoxybenzoic acid could not be obtained in a high yield (Entry 5, Table 9). On the other hand, *p*-nitrobenzoic acid was produced in 91% yield by the oxidation using a 4 molar amount of 30% H_2O_2 followed by treatment with an aqueous solution of $Na_2S_2O_3$ (Entry 10, Table 9).

Conclusion

We devised a practical method for converting alcohols into the corresponding carbonyl compounds with aqueous H_2O_2, an ideal oxidant. The catalyst system typically consists of sodium tungstate and methyltrioctylammonium hydrogensulfate. The biphasic oxidation can be carried out at 70—90 °C with a substrate-to-catalyst ratio of 50—500 without organic solvents or, if necessary, by adding toluene. Hazardous halogenated solvents are not required. The organic/aqueous biphasic system allows simple work-up and easy catalyst/substrate separation. No technical problems are foreseen for a large-scale reaction. Secondary alcohols are converted to ketones, whereas primary alcohols are oxidized to aldehydes or carboxylic acids by selecting appropriate reaction parameters. Many polar functional groups tolerate under the oxidation conditions. This procedure is simple, effective, and environment-conscious, meeting with all the requirements of modern organic synthesis. The utility has been highlighted by the direct oxidation of cyclohexene to crystalline adipic acid.[55]

Experimental

General. ^{1}H and ^{13}C NMR spectra were measured on a JEOL JNM-A400 NMR spectrometer at 400 and 100 MHz, respectively. The chemical shifts of ^{1}H NMR spectra are reported in ppm on δ scale downfield from tetramethylsilane used as an internal standard, and signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad peak. The chemical shifts of ^{13}C NMR spectra are reported in ppm with chloroform-*d* ($\delta = 77.00$) as an internal standard. Elemental analyses were performed on a LECO CHN-900 analyzer. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-600H or JMS-700 mass spectrometer. Melting points were determined on a Yanako MP-J3 apparatus and are uncorrected. Gas chromatographic (GC) analyses were carried out using a Shimadzu GC-14A or a 17A gas chromatograph furnished with an OV-1 column (0.25 mm×50 m, GL Sciences Inc.) and helium (1.2 kg cm^{-2}) as carrier gas, unless otherwise stated. High-performance liquid chromatographic (HPLC) analyses were performed on a JASCO 880-PU liquid chromatograph using a Develosil ODS-5 column (4.6 mm×25 cm, Nomura Chemical).

Materials. Tungstic acid, sodium tungstate dihydrate, aqueous 30% hydrogen peroxide, phosphoric acid, *N*-hexadecylpyridinium chloride, tetrabutylammonium chloride, tetrabutylammonium hydrogensulfate, and (−)-menthol were obtained from Nacalai Tesque, Inc., and were used as received. 2-Propanol, cyclopentanol, cyclohexanol, benzyl alcohol, 1-phenylethanol, 2-ethyl-1,3-hexanediol, 2-methylcyclohexanone, 1-octene, toluene, and 5,6-dihydro-2*H*-pyrane were obtained from Nacalai Tesque, Inc., and were distilled before use. 4-*t*-Butylcyclohexanol, (±)-borneol, tetrakis(decyl)ammonium hydroxide, tetrahexylammonium hydroxide, methyltrioctylammonium chloride, and *t*-butyldimethylsilyl chloride were obtained from Tokyo Kasei Kogyo Co., Ltd., and were used as received. 2-Pentanol, 1-octanol, 2-octanol, 2-ethyl-1-hexanol, 1-nonanol, 1,2-epoxydodecane, dioctyl ether, (*Z*)-3-octene, (*E*)-3-octene, 2-methyl-1-undecene, 2-decanone, and nonanal were purchased from Tokyo Kasei Kogyo Co., Ltd., and were distilled before use. 6-Oxoheptanoic acid, *o*-bromobenzoic acid, and triphenylmethyl chloride were obtained from Aldrich Chemical Co., and were used as received. Tetrakis(decyl)ammonium hydrogensulfate and tetrahexylammonium hydrogensulfate were prepared from sulfuric acid and the corresponding ammonium hydroxide. Methyltrioctylammonium sulfate was synthesized from methyltrioctylammonium chloride and sodium sulfate. 2-Methyl-2-decene was prepared by the Wittig reaction. 3,4-Diethyl-3-hexene was prepared from the reductive coupling[56] of 3-pentanone. A convenient method for preparation of methyltrioctylammonium hydrogensulfate was given in Ref. 42a. (Aminomethyl)phosphonic acid[57] was synthesized according to the literature. 1-(*o*-Bromophenyl)-2-methyl-1-propanol was obtained by the reaction of isopropylmagnesium bromide and *o*-bromobenzoyl chloride, which was synthesized from *o*-bromobenzoic acid. 9,11-Nonadecanediol was obtained by the sodium borohydride reduction of 11-hydroxy-9-nonadecanone prepared from 2-decanone and nonanal. Ethyl 6-hydroxyheptanoate was prepared from the esterification of 6-oxoheptanoic acid with ethanol, followed by the reduction with sodium borohydride. 7-(Triphenylmethoxy)-2-heptanol, 7-(*t*-butyldimethylsilyloxy)-2-heptanol, and 7-(tetrahydro-2-pyranyloxy)-2-heptanol were synthesized from 1,6-heptanediol and triphenylmethyl chloride, *t*-butyldimethylsilyl chloride, and 5,6-dihydro-2*H*-pyrane, respectively. 1,6-Heptanediol was obtained by the reduction of methyl 6-oxoheptanoate with lithium aluminum hydride. *N*-Hexyl-6-hydroxyheptanamide was prepared by the amidation of 6-oxoheptanoic acid with hexylamine, followed by the reduction with sodium borohydride.

1-(*o*-Bromophenyl)-2-methyl-1-propanol: ^{1}H NMR (400 MHz, CDCl$_3$) $\delta = 0.95$ (d, 3H, $J = 6.8$ Hz), 0.96 (d, 3H, $J = 6.8$ Hz), 1.97 (d, 1H, $J = 2.9$ Hz), 2.06 (qqd, 1H, $J = 6.8$, 6.8, 5.9 Hz), 4.86 (dd, 1H, $J = 2.9$, 5.9 Hz), 7.11 (dt, 1H, $J = 2.0$, 7.3 Hz), 7.32 (t, 1H, $J = 7.3$ Hz), 7.48—7.53 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) $\delta = 16.74$, 19.43, 33.92, 77.48, 122.60, 127.36, 128.21, 128.60, 132.58, 142.85. HRMS (FAB$^+$) *m*/*z* Calcd for $C_{10}H_{13}BrNaO$: ([M + Na]$^+$), 251.0048. Found: *m*/*z* 251.0031.

9,11-Nonadecanediol: ^{1}H NMR (400 MHz, CDCl$_3$) $\delta = 0.88$ (t, 6H, $J = 6.8$ Hz), 1.27—1.48 (m, 30H), 3.81—3.97 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) $\delta = 14.00$, 22.59, 25.32, 29.23, 29.53, 29.62, 31.82, 38.15, 42.67, 73.08. HRMS (FAB$^+$) *m*/*z* Calcd for $C_{19}H_{40}NaO_2$: ([M + Na]$^+$), 323.2926. Found: *m*/*z* 323.2913.

Ethyl 6-Hydroxyheptanoate: ^{1}H NMR (400 MHz, CDCl$_3$) $\delta = 1.19$ (d, 3H, $J = 5.9$ Hz), 1.26 (t, 3H, $J = 7.5$ Hz), 1.35—1.67 (m, 7H), 2.31 (t, 2H, $J = 7.3$ Hz), 3.68—3.81 (m, 1H), 4.13 (q, 2H, $J = 7.5$ Hz). ^{13}C NMR (100 MHz, CDCl$_3$) $\delta = 14.17$, 23.44, 24.80, 25.21, 34.21, 38.80, 60.18, 67.71, 173.70. HRMS (FAB$^+$) *m*/*z* Calcd for $C_9H_{19}O_3$: ([M + H]$^+$), 175.1334. Found: *m*/*z* 175.1344.

7-(Triphenylmethoxy)-2-heptanol: ^{1}H NMR (400 MHz, CDCl$_3$) $\delta = 1.16$ (d, 3H, $J = 6.0$ Hz), 1.24—1.65 (m, 9H), 3.05 (t, 2H, $J = 6.3$ Hz), 3.76 (tq, 1H, $J = 6.0$, 6.0 Hz), 7.21 (tt, 3H, $J = 1.5$, 7.3 Hz), 7.27—7.31 (m, 6H), 7.43—7.45 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) $\delta = 23.47$, 25.59, 26.27, 29.98, 39.28, 63.47, 68.09, 86.29, 126.79, 127.67, 128.68, 144.49. HRMS (FAB$^+$) *m*/*z* Calcd for $C_{26}H_{30}NaO_2$: ([M + Na]$^+$), 397.2144. Found: *m*/*z* 397.2135.

7-(*t*-Butyldimethylsilyloxy)-2-heptanol: ^{1}H NMR (400 MHz, CDCl$_3$) $\delta = 0.04$ (s, 6H), 0.89 (s, 9H), 1.19 (d, 3H, $J = 5.9$ Hz), 1.33—1.54 (m, 9H), 2.60 (t, 2H, $J = 6.3$ Hz), 3.79—3.80 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) $\delta = 5.28$, 18.36, 23.49, 25.55, 25.84, 25.97, 32.80, 39.35, 63.16, 68.10. HRMS (FAB$^+$) *m*/*z* Calcd for $C_{13}H_{31}O_2Si$: ([M + H]$^+$), 247.2093. Found: *m*/*z* 247.2066.

7-(Tetrahydro-2-pyranyloxy)-2-heptanol: ^{1}H NMR (400 MHz, CDCl$_3$) $\delta = 1.19$ (d, 3H, $J = 6.3$ Hz), 1.40—1.86 (m, 15H), 3.39 (td, 1H, $J = 6.8$, 9.3 Hz), 3.47—3.51 (m, 1H), 3.71—3.89 (m, 3H), 4.56—4.57 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) $\delta = 19.59$, 19.62, 23.40, 25.41, 25.47, 25.51, 26.15, 26.21, 29.60, 29.62, 30.69, 39.19, 62.25, 62.28, 67.42, 67.46, 67.85, 98.77, 98.78. HRMS (FAB$^+$) *m*/*z* Calcd for $C_{12}H_{25}O_3$: ([M + H]$^+$), 217.1804. Found: *m*/*z* 217.1814

***N*-Hexyl-6-hydroxyheptanamide:** ^{1}H NMR (400 MHz, CDCl$_3$) $\delta = 0.89$ (t, 3H, $J = 7.3$ Hz), 1.18 (d, 3H, $J = 6.3$ Hz), 1.29—1.78 (m, 15H), 2.17 (t, 2H, $J = 7.3$ Hz), 3.23 (dt, 2H, $J = 6.7$, 6.7 Hz), 3.80—3.81 (m, 1H), 5.52 (br, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) $\delta = 13.97$, 22.52, 23.53, 25.33, 25.54, 26.56, 29.61, 31.45, 36.66, 38.83, 39.50, 67.74, 172.86. HRMS (FAB$^+$) *m*/*z* Calcd for $C_{13}H_{28}NO_2$: ([M + H]$^+$), 230.2120. Found: *m*/*z* 230.2144.

Procedure for Oxidation of 2-Octanol: General Procedure for the 100-g Scale Oxidation and Reuse of the Water Phase and Distillation Residue. The First Run (General Procedure): A 500-mL, round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with 0.507 g (1.54 mmol) of $Na_2WO_4 \cdot 2H_2O$, 0.717 g (1.54 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 95.8 g (845 mmol) of aqueous 30% H_2O_2. The biphasic mixture was vigorously stirred at room temperature for 10 min, and then 100 g (768 mmol) of 2-octanol was added. The mixture was heated at 90 °C for 4 h with stirring at 1000 rpm, and then cooled to room temperature. The organic phase was separated, washed with 100 mL of saturated aqueous $Na_2S_2O_3$, and distilled through a short column to give 93.9 g (95%) of 2-octanone as a colorless liquid, bp 173.0—173.3 °C.

The Second Run: A 1-L, round-bottomed flask was charged with the water phase of the 1st run containing the W catalyst, 0.717 g (1.54 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, 95.8 g (844 mmol) of aqueous 30% H_2O_2, and distillation residue of the 1st run containing some ammonium salt. After the mixture was vigorously stirred at room temperature for 10 min, 100 g (768 mmol) of 2-octanol was added. This mixture was heated at 90 °C for 10 h with stirring at 1000 rpm, and then cooled to room temperature. The organic phase was separated, washed, and distilled to give 84.7 g (86%) of 2-octanone.

The Third Run: The 1-L, round-bottomed flask was placed with the water phase of the 2nd run, 0.717 g (1.54 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, 95.8 g (844 mmol) of aqueous 30% H_2O_2, and distillation residue of the 2nd run. The biphasic mixture was vigorously stirred at room temperature for 10 min, and then 100 g (768 mmol) of 2-octanol was added. This mixture was heated at 90 °C for 24 h with stirring at 1000 rpm, and then cooled to room temperature. The organic phase was separated, washed, and distilled to give 90.6 g (92%) of 2-octanone.

Procedure for Oxidation of Benzyl Alcohol to Benzaldehyde: General Procedure for the 100-g Scale Oxidation. A 500-mL, three-necked, round-bottomed flask equipped with a magnetic stirring bar, a reflux condenser, a thermometer, and a 100-mL dropping funnel was charged with 914 mg (2.77 mmol) of $Na_2WO_4 \cdot 2H_2O$, 1.29 g (2.77 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 62.9 g (92.5 mmol) of aqueous 5% H_2O_2. After the mixture was vigorously stirred at room temperature for 10 min, 100 g (925 mmol) of benzyl alcohol was added. Then the whole mixture was heated at 90 °C for 10 min with stirring at 1000 rpm; next 105 g (925 mmol) of aqueous 30% H_2O_2 was added dropwise via the dropping funnel over a period of 3 h. After this mixture was cooled to room temperature, the organic phase was separated, washed with 50 mL of saturated aqueous $Na_2S_2O_3$, and distilled through a 15-cm Vigreux column to give 85.8 g (87%) of benzaldehyde as a colorless liquid, bp 81.0—82.0 °C/28 mmHg (1 mmHg = 133.322 Pa). This procedure was improved from that reported earlier.[39]

Procedure for Determining the Turnover Number of the Catalytic Oxidation. Oxidation of 2-Octanol: A 300-mL, round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with 1.67 mg (5.07 μmol) of $Na_2WO_4 \cdot 2H_2O$, 0.233 g (0.500 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 170 g (1.50 mol) of aqueous 30% H_2O_2. The biphasic mixture was vigorously stirred at room temperature for 10 min, and then 127.8 g (0.982 mol) of 2-octanol and 12.42 g (96.87 mmol) of nonane as internal standard were added. This mixture was heated at 90 °C for 126 h with stirring at 1000 rpm. The yield of 2-octanone was determined to be 40.1% by GC analysis of small aliquots of the organic phase. The GC data were corrected for the relative response of the detector by integrating the response of each analyte against nonane. GC (column, OV-1, 0.25 mm×50 m, GL Sciences Inc.); carrier gas, helium (1.2 $kg\,cm^{-2}$); initial column temp, 70 °C; final column temp, 280 °C; progress rate, 5 $°C\,min^{-1}$; injection temp, 280 °C; split ratio, 100 : 1; retention time (t_R) of nonane, 8.2 min; t_R of 2-octanone, 9.8 min; t_R of 2-octanol, 10.3 min.

Oxidation of 2-Phenylethanol: A 1-L, round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with 1.651 mg (5.005 μmol) of $Na_2WO_4 \cdot 2H_2O$, 0.466 g (1.00 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 227 g (2.00 mol) of aqueous 30% H_2O_2. The biphasic mixture was vigorously stirred at room temperature for 10 min, and then 243.5 g (1.993 mol) of 2-phenylethanol and 15.65 g (100.1 mmol) of undecane as internal standard were added. This mixture was heated at 90 °C for 240 h with stirring at 1000 rpm. The yield of acetophenone was determined to be 45.0% by GC analysis of small aliquots of the organic phase. The GC data were corrected for the relative response of the detector by integrating the response of each analyte against undecane. GC (column, DB-WAX, 0.25 mm×15 m, J&W Scientific); carrier gas, helium (1.2 $kg\,cm^{-2}$); column temp, 100 °C; injection temp, 200 °C; split ratio, 100 : 1; t_R of undecane, 0.6 min; t_R of acetophenone, 4.9 min; t_R of 2-phenylethanol, 11.6 min.

Oxidation of 1-Octanol: A 20-mL, round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with 0.33 mg (1.0 μmol) of $Na_2WO_4 \cdot 2H_2O$, 4.7 mg (10 μmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 4.53 g (40 mmol) of aqueous 30% H_2O_2. After the mixture was vigorously stirred at room temperature for 10 min, 2.60 g (20 mmol) of 1-octanol and 0.8066 g (4.472 mmol) of tridecane as internal standard were added. This mixture was heated at 90 °C for 36 h with stirring at 1000 rpm. Octanoic acid was analyzed after conversion to the methyl ester by adding an excess amount of trimethylsilyldiazomethane to small aliquots of the organic phase. The GC data were corrected by integrating the response of each analyte against tridecane, indicating the yield to be 14.6%. GC (column, OV-1, 0.25 mm×50 m, GL Sciences Inc.); carrier gas, helium (1.2 $kg\,cm^{-2}$); initial column temp, 80 °C; final column temp, 280 °C; progress rate, 15 $°C\,min^{-1}$; injection temp, 280 °C; split ratio, 100 : 1; t_R of 1-octanol, 7.9 min; t_R of methyl octanoate, 8.2 min; t_R of tridecane, 10.4 min.

General Procedure for Relative Rate Study. A 20-mL, round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with 6.6 mg (0.02 mmol) of $Na_2WO_4 \cdot 2H_2O$, 18.6 mg (0.04 mmol) of $[CH_3\,(n\text{-}C_8H_{17})_3N]HSO_4$, and 6.78 g (10 mmol) of aqueous 5% H_2O_2. After the mixture was stirred at 1000 rpm at room temperature for 10 min, a mixture of 5 mmol of each substrate and 1 mmol of an internal standard (typically nonane) were added. This mixture was heated to 110 °C with stirring at 1000 rpm for 0.67—5 h. The disappearance of the substrates was monitored at low conversion to ensure that the concentration of the oxidant did not change appreciably during the reaction. The GC data were corrected for the relative response of the detector by integrating the response of each analyte against the internal standard.

Hammett Plot for Oxidation of *p*-Substituted Benzyl Alcohols. A 20-mL, round-bottomed flask equipped with a magnetic stirring bar was charged with 8.2 mg (0.025 mmol) of $Na_2WO_4 \cdot 2H_2O$, 11.6 mg (0.025 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 6.78 g (10 mmol) of aqueous 5% H_2O_2. After the mixture was stirred at 1000 rpm at room temperature for 10 min, a mixture of 541 mg (5.0 mmol) of benzyl alcohol and 5.0 mmol of *p*-substituted benzyl alcohol in toluene (2 mL) was added. This mixture was heated to 50 °C with stirring at 1000 rpm for 5—6 min, then 338 mg (1.70 mmol) of tetradecane as internal standard was added. The conversion of substrates was thus kept below 10%. The disappearance of the substrates was monitored by GC analysis of small aliquots of the organic phase. The GC data were corrected by integrating the response of each analyte against tetradecane. Initial relative rates (v_X/v_H) thus determined were 1.66 (*p*-OCH_3), 1.20 (*p*-CH_3), 1.00 (*p*-H), 0.88 (*p*-Cl), and 0.86 (*p*-Br), respectively.

2-Pentanone. Bp 100.0—105.0 °C. ^1H NMR (400 MHz, $CDCl_3$) $\delta = 0.92$ (t, 3H, $J = 7.6$ Hz), 1.56—1.65 (m, 2H), 2.13

(s, 3H), 2.41 (t, 2H, $J = 7.2$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 13.62, 17.24, 29.80, 45.63, 209.18$. HRMS (EI$^+$) *m*/*z* Calcd for $C_5H_{10}O$: (M$^+$), 86.0732. Found: *m*/*z* 86.0705.

2-Octanone. Bp 173.0—173.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.88$ (t, 3H, $J = 6.8$ Hz), 1.27—1.29 (m, 6H), 1.52—1.59 (m, 2H), 2.13 (s, 3H), 2.42 (t, 2H, $J = 7.3$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 13.93, 22.42, 23.77, 28.78, 29.74, 31.52, 43.73, 209.23$. HRMS (EI$^+$) *m*/*z* Calcd for $C_8H_{16}O$: (M$^+$), 128.1201. Found: *m*/*z* 128.1192.

2-Undecanone. Bp 138.5—139.0 °C/30 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.88$ (t, 3H, $J = 7.2$ Hz), 1.21—1.32 (m, 12H), 1.53—1.60 (m, 2H), 2.13 (s, 3H), 2.42 (t, 2H, $J = 7.6$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 14.02, 22.60, 23.81, 29.12, 29.20, 29.34, 29.37, 29.76, 31.80, 43.75, 209.25$. HRMS (EI$^+$) *m*/*z* Calcd for $C_{11}H_{22}O$: (M$^+$), 170.1671. Found: *m*/*z* 170.1644.

Cyclopentanone.[58] Bp 128.0—132.5 °C. The reaction was run for 16 h. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.94$—2.00 (m, 4H), 2.14—2.20 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 23.06, 38.17, 220.47$.

Cyclohexanone. Bp 155.0—156.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.70$—1.75 (m, 2H), 1.85—1.93 (m, 4H), 2.34 (t, 4H, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 24.82, 26.85, 41.79, 211.92$. HRMS (EI$^+$) *m*/*z* Calcd for $C_6H_{10}O$: (M$^+$), 98.0732. Found: *m*/*z* 98.0705.

4-*t*-Butylcyclohexanone.[59] The reaction was run in a manner identical with the procedure for Oxidation of 2-Octanol, except that 100 mL of toluene was used as solvent. Bp 116.0—118.0 °C/20 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.92$ (s, 9H), 1.42—1.50 (m, 3H), 2.07—2.11 (m, 2H), 2.27—2.42 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 27.58, 27.59, 32.45, 41.30, 46.71, 212.50$.

2-*t*-Butylcyclohexanone. A 20-mL flask was charged with 13.2 mg (0.04 mmol) of $Na_2WO_4\cdot 2H_2O$, 18.6 mg (0.04 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 2.72 g (24 mmol) of aqueous 30% H_2O_2. After the mixture was vigorously stirred at room temperature for 10 min, 3.13 g (20 mmol) of 2-*t*-butylcyclohexanol (a mixture of *cis* and *trans* isomer) was added. This mixture was heated at 90 °C for 4 h with stirring at 1000 rpm. The organic phase was separated, washed with 5 mL of saturated aqueous $Na_2S_2O_3$, and chromatographed on silica gel (BW 300, 100 g; eluent, 10 : 1 hexane–ether) to give 2.40 g (78%) of 2-*t*-butylcyclohexanone as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.99$ (s, 9H), 1.42—1.52 (m, 1H), 1.57—1.70 (m, 2H), 1.87—1.92 (m, 1H), 2.12—2.21 (m, 2H), 2.27—2.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 25.99, 27.64, 28.59, 29.79, 31.83, 44.20, 60.20, 212.83$. HRMS (EI$^+$) *m*/*z* Calcd for $C_{10}H_{18}O$: (M$^+$), 154.1358. Found: *m*/*z* 154.1339.

2,6-Dimethylcyclohexanone. A mixture of 13.2 mg (0.04 mmol) of $Na_2WO_4\cdot 2H_2O$, 18.6 mg (0.04 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 2.72 g (24 mmol) of aqueous 30% H_2O_2 was vigorously stirred at room temperature for 10 min. To this was added 2.56 g (20 mmol) of 2,6-dimethylcyclohexanol (a stereoisomeric mixture); then the mixture was heated at 90 °C for 4 h with stirring at 1000 rpm. The organic phase was separated, washed with 5 mL of saturated aqueous $Na_2S_2O_3$, and chromatographed on silica gel (BW 300, 100 g; eluent, 4 : 1 hexane–ether) to give 2.12 g (84%) of 2,6-dimethylcyclohexanone (a 4 : 1 mixture of diastereoisomers) as a colorless liquid. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.01$ (d, 6H, $J = 6.0$ Hz), 1.29—1.40 (m, 2H), 1.74—1.81 (m, 2H), 2.08—2.14 (m, 2H), 2.40 (tqd, 2H, $J = 12.0, 6.0, 6.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 14.52, 25.54, 37.22, 45.30, 214.52$. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.10$ (d, 6H, $J = 7.2$ Hz), 1.57 (m, 2H), 1.74—1.81 (m, 2H), 1.92—1.97 (m, 2H), 2.58 (qt, 2H, $J = 7.2, 7.2$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 15.94, 20.14, 34.70, 42.64, 217.24$. HRMS (EI$^+$) *m*/*z* Calcd for $C_8H_{14}O$: (M$^+$), 126.1045. Found: *m*/*z* 126.1018.

2,2,4,4-Tetramethylpentan-3-one. The reaction was performed under conditions similar to the procedure for Oxidation of 2-Octanol, except that 1040 g (919 mmol) of aqueous 3% H_2O_2 was used. Bp 150.0—155.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.25$ (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 28.58, 45.68, 218.91$. HRMS (EI$^+$) *m*/*z* Calcd for $C_9H_{18}O$: (M$^+$), 142.1358. Found: *m*/*z* 142.1367.

Acetophenone.[60] The reaction was run for 1 h. Bp 85.5—88.0 °C/20 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 2.60$ (s, 3H), 7.44 (dd, 2H, $J = 7.2, 8.0$ Hz), 7.55 (t, 1H, $J = 8.0$ Hz), 7.94 (d, 2H, $J = 7.2$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 26.54, 128.24, 128.51, 133.04, 137.09, 198.06$.

***o*-Bromoisobutyrophenone.** The product was obtained by a reaction using a 20-mL flask, 4.6 mg (0.014 mmol) of $Na_2WO_4\cdot 2H_2O$, 6.4 mg (0.014 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, 469.5 mg (4.14 mmol) of aqueous 5% H_2O_2, and 633 mg (2.76 mmol) of 1-(*o*-bromophenyl)-2-methyl-1-propanol. After heating and stirring, the organic phase was chromatographed on silica gel (BW 300, 30 g; eluent, 15 : 1 hexane–ether) to give 588 mg (94%) of *o*-bromoisobutyrophenone as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.20$ (d, 6H, $J = 6.83$ Hz), 3.33 (m, 1H, $J = 6.83$ Hz), 7.26—7.29 (m, 2H), 7.34—7.38 (m, 1H), 7.58—7.61 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 18.08, 40.15, 118.63, 127.21, 128.09, 131.02, 133.36, 142.02, 208.66$. HRMS (EI$^+$) *m*/*z* Calcd for $C_{10}H_{11}BrO$: (M$^+$), 225.9994. Found: *m*/*z* 225.9968.

2-Ethyl-1-hydroxy-3-hexanone.[33] Bp 90.9—99.0 °C/1 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.92$ (t, 6H, $J = 7.2$ Hz), 1.48—1.69 (m, 4H), 2.31 (t, 1H, $J = 7.2$ Hz), 2.48 (t, 2H, $J = 7.2$ Hz), 2.63—2.66 (m, 1H), 3.69 (dd, 1H, $J = 4.1, 11.2$ Hz), 3.79 (dd, 1H, $J = 7.6, 11.2$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 11.68, 13.61, 16.71, 21.23, 44.77, 55.03, 62.42, 215.11$.

Oxidation of 9,11-Nonadecanediol. A 20-mL flask was charged with 13.2 mg (0.04 mmol) of $Na_2WO_4\cdot 2H_2O$, 18.6 mg (0.04 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 4.08 g (6.0 mmol) of aqueous 5% H_2O_2. After the mixture was vigorously stirred at room temperature for 10 min, 601 mg (2.0 mmol) of 9,11-nonadecanediol and 1 mL of toluene were added. This mixture was heated at 90 °C for 4 h with stirring at 1000 rpm. The organic phase was separated, washed with 5 mL of saturated aqueous $Na_2S_2O_3$, and chromatographed on silica gel (BW 300, 60 g; eluent, 100 : 1 to 1 : 1 hexane–ether) to give 435 mg (73%) of 11-hydroxynonadecan-9-one and 82.1 mg (14%) of 9,11-nonadecanediol as white crystals, and 58.5 mg (10%) of 9,11-nonadecanedione as pale yellow crystals.

11-Hydroxynonadecan-9-one: ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.88$ (t, 6H, $J = 6.8$ Hz), 1.27—1.59 (m, 26H), 2.42 (d, 2H, $J = 7.3$ Hz), 2.59 (dd, 1H, $J = 17.3, 2.9$ Hz), 2.49 (dd, 1H, $J = 17.3, 9.3$ Hz), 3.12 (m, 1H), 4.02 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 14.06, 14.07, 22.62, 22.64, 23.62, 25.46, 29.09, 29.15, 29.23, 29.32, 29.53, 29.56, 31.79, 31.85, 36.45, 43.68, 48.91, 67.65, 212.65$. HRMS (EI$^+$) *m*/*z* Calcd for $C_{19}H_{38}O_2$: (M$^+$), 298.2872. Found: *m*/*z* 298.2896.

9,11-Nonadecanedione: ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.88$ (t, 3H, $J = 6.3$ Hz), 1.22—1.63 (m, 24H), 2.27 (t, 3.3H, $J = 7.3$ Hz), 2.49 (t, 0.6H, $J = 7.8$ Hz), 3.54 (s, 0.3H), 5.47 (s, 0.8H). Enol form: ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 14.05, 22.61, 25.71, 29.11, 29.22, 29.29, 31.79, 38.38, 99.01, 194.52$. Keto form: ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 14.04, 22.61, 23.37, 29.01, 29.08, 29.30, 31.77, 43.78, 57.18, 204.41$. HRMS (EI$^+$) *m*/*z* Calcd for $C_{19}H_{36}O_2$: (M$^+$), 296.2715. Found: *m*/*z* 296.2738.

(±)-Camphor. The reaction was performed with 100 mL of toluene. Bp 204.0—205.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.85$ (s, 3H), 0.92 (s, 3H), 0.97 (s, 3H), 1.31—1.45 (m, 2H), 1.69 (ddd, 1H, $J = 4.0$, 12.4, 13.2 Hz), 1.85 (d, 1H, $J = 18.3$ Hz), 1.96 (dddd, 1H, $J = 4.0$, 4.0, 12.4, 18.1 Hz), 2.10 (dd, 1H, $J = 4.0$, 4.0 Hz), 2.36 (ddd, 1H, $J = 4.0$, 4.0, 18.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 9.22$, 19.12, 19.76, 27.03, 29.90, 43.05, 43.28, 46.76, 57.67, 219.62. HRMS (EI$^+$) *m/z* Calcd for $C_{10}H_{16}O$: (M^+), 152.1201. Found: *m/z* 152.1172.

(−)-Menthone. Bp 70.0—72.0 °C/1 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.85$ (d, 3H, $J = 6.8$ Hz), 0.91 (d, 3H, $J = 6.8$ Hz), 1.01 (d, 3H, $J = 6.3$ Hz), 1.32—1.40 (m, 2H), 1.88—2.15 (m, 6H), 2.32—2.37 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta =$ 18.65, 21.17, 22.24, 25.86, 27.83, 33.91, 35.42, 50.83, 55.85, 212.33. HRMS (EI$^+$) *m/z* Calcd for $C_{10}H_{18}O$: (M^+), 154.1358. Found: *m/z* 154.1337. The product was 99.3% stereochemically pure. Upon prolonged exposure to the reaction conditions, it slowly isomerized to give a mixture of (−)-menthone and (+)-isomenthone. GC (column, OV-1, 0.25 mm×50 m, GL Sciences Inc.); carrier gas, helium (1.2 kg cm^{-2}); initial column temp, 90 °C; final column temp, 180 °C; progress rate, 15 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of (−)-menthone, 5.0 min; t_R of (+)-isomenthone, 5.6 min.

Ethyl 6-Oxoheptanoate. The reaction was performed under conditions similar to the procedure for Oxidation of 2-Octanol, except that 33.0 mg (0.10 mmol) of $Na_2WO_4 \cdot 2H_2O$, 46.6 mg (0.10 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, 8.16 g (12 mmol) of aqueous 5% H_2O_2, and 2 mL of toluene were used. The product was isolated by column chromatography on silica gel (BW 300, 60 g; eluent, 1 : 1 hexane–ether). Ethyl 6-hydroxyheptanoate was recovered in 9% yield. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.25$ (t, 3H, $J = 7.3$ Hz), 1.60—1.63 (m, 4H), 2.14 (s, 3H), 2.31 (t, 2H, $J = 7.1$ Hz), 2.45 (t, 2H, $J = 7.1$ Hz), 4.12 (q, 2H, $J = 7.3$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 14.20$, 23.16, 24.37, 29.84, 34.03, 43.24, 60.25, 173.36, 208.47. HRMS (FAB$^+$) *m/z* Calcd for $C_9H_{17}O_3$: ([M + H]$^+$), 173.1178. Found: *m/z* 173.1156.

7-(Triphenylmethoxy)-2-heptanone. The reaction was run in a manner identical with the procedure for Oxidation of 2-Octanol, except that 33.0 mg (0.10 mmol) of $Na_2WO_4 \cdot 2H_2O$, 46.6 mg (0.10 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, 8.16 g (12 mmol) of aqueous 5% H_2O_2, and 2 mL of toluene were used. The product was isolated by column chromatography on silica gel (BW 300, 100 g; eluent, 6 : 1 to 2 : 1 hexane–ether). 7-(Triphenylmethoxy)-2-heptanol was recovered in 7% yield. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.32$—1.40 (m, 2H), 1.54 (tt, 2H, $J = 7.3$, 7.3 Hz), 1.59 (tt, 2H, $J = 6.5$, 6.5 Hz), 2.10 (s, 3H), 2.39 (t, 2H, $J = 7.3$ Hz), 3.05 (t, 2H, $J = 6.5$ Hz), 7.20—7.24 (m, 3H), 7.28 (dd, 6H, $J = 7.3$, 7.3 Hz), 7.43 (d, 6H, $J = 7.3$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 23.56$, 25.77, 29.70, 29.71, 43.54, 63.23, 86.21, 126.72, 127.58, 128.55, 144.32, 208.88. HRMS (FAB$^+$) *m/z* Calcd for $C_{26}H_{28}NaO_2$: ([M + Na]$^+$), 395.1987. Found: *m/z* 395.1978.

7-(*t*-Butyldimethylsilyloxy)-2-heptanone. The reaction was run using 33.0 mg (0.10 mmol) of $Na_2WO_4 \cdot 2H_2O$, 46.6 mg (0.10 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, 8.16 g (12 mmol) of aqueous 5% H_2O_2, and 2 mL of toluene. The product was isolated by column chromatography on silica gel (BW 300, 70 g; eluent, 5 : 1 to 3 : 1 hexane–ether). 7-(*t*-Butyldimethylsilyloxy)-2-heptanol was recovered in 17% yield. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.04$ (s, 6H), 0.89 (s, 9H), 1.30—1.37 (m, 2H), 1.48—1.53 (m, 2H), 1.59 (tt, 2H, $J = 7.3$, 7.3 Hz), 2.13 (s, 3H), 2.43 (t, 2H, $J = 7.3$ Hz), 3.60 (t, 2H, $J = 6.6$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = -5.30$, 18.34, 23.64, 25.44, 25.95, 29.85, 32.58, 43.76, 62.95, 209.13. HRMS (FAB$^+$) *m/z* Calcd for $C_{13}H_{29}O_2Si$: ([M + H]$^+$), 245.1937. Found: *m/z* 245.1932.

Oxidation of 7-(Tetrahydro-2-pyranyloxy)-2-heptanol. A 20-mL flask was charged with 33.0 mg (0.10 mmol) of $Na_2WO_4 \cdot 2H_2O$, 46.6 mg (0.10 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 10.2 g (15 mmol) of aqueous 5% H_2O_2. After the mixture was vigorously stirred at room temperature for 10 min, 2.16 g (10 mmol) of 7-(tetrahydro-2-pyranyloxy)-2-heptanol and 2 mL of toluene were added. This mixture was heated at 90 °C for 2 h with stirring at 1000 rpm. The organic phase was separated, washed with 5 mL of saturated aqueous $Na_2S_2O_3$, and chromatographed on silica gel (BW 300, 70 g; eluent, 30 : 1 to 3 : 1 hexane–acetone) to give 258 mg (12%) of 7-(tetrahydro-2-pyranyloxy)-2-heptanone, 86.6 mg (4%) of 7-(tetrahydro-2-pyranyloxy)-2-heptanol, 354 mg (27%) of 7-hydroxy-2-heptanone, and 141 mg (11%) of 1,6-heptanediol as a colorless liquid. The aqueous phase was extracted with ethyl acetate (3×10 mL) to give additional 314 mg (24%) of 7-hydroxy-2-heptanone and 165 mg (12%) of 1,6-heptanediol.

7-(Tetrahydro-2-pyranyloxy)-2-heptanone: ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.33$—1.87 (m, 12H), 2.14 (s, 3H), 2.14 (s, 3H), 2.44 (t, 2H, $J = 7.5$ Hz), 3.38 (td, 1H, $J = 6.5$, 9.8 Hz), 3.48—3.51 (m, 1H), 3.73 (td, 1H, $J = 6.8$, 9.8 Hz), 3.83—3.89 (m, 1H), 4.55—4.57 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 19.62$, 23.56, 25.40, 25.77, 29.44, 29.76, 30.68, 43.58, 62.30, 67.25, 98.82, 208.94. HRMS (FAB$^+$) *m/z* Calcd for $C_{12}H_{23}O_3$: ([M + H]$^+$), 215.1647. Found: *m/z* 215.1658.

7-Hydroxy-2-heptanone: ^{1}H NMR (400 MHz, $CDCl_3$) $\delta =$ 1.33—1.40 (m, 2H), 1.54—1.62 (m, 4H), 2.14 (s, 3H), 2.19 (br, 1H), 2.45 (t, 2H, $J = 7.3$ Hz), 3.63 (t, 2H, $J = 5.9$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 23.35$, 25.20, 29.80, 32.29, 43.52, 62.35, 209.32. HRMS (FAB$^+$) *m/z* Calcd for $C_7H_{14}NaO_2$: ([M + Na]$^+$), 153.0892. Found: *m/z* 153.0916.

1,6-Heptanediol: ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.19$ (s, 3H, $J = 6.3$ Hz), 1.36—1.62 (m, 10H), 3.65 (t, 2H, $J = 6.3$ Hz), 3.77—3.83 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 23.00$, 24.02, 29.82, 33.68, 43.14, 179.05, 208.95. HRMS (EI$^+$) *m/z* Calcd for $C_7H_{16}O_2$: (M^+), 132.1150. Found: *m/z* 132.1144.

***N*-Hexyl-6-oxoheptanamide.** The reaction was run under conditions similar to the procedure for Oxidation of 2-Octanol, except that 33.0 mg (0.10 mmol) of $Na_2WO_4 \cdot 2H_2O$, 46.6 mg (0.10 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, 8.16 g (12 mmol) of aqueous 5% H_2O_2, and 2 mL of toluene were used. The product was isolated by column chromatography on silica gel (BW 300, 60 g; eluent, 3 : 1 hexane–acetone). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.88$ (t, 3H, $J = 6.8$ Hz), 1.26—1.72 (m, 12H), 2.14 (s, 3H), 2.17—2.20 (m, 2H), 2.47 (t, 2H, $J = 6.6$ Hz), 3.23 (dt, 2H, $J = 5.9$, 7.3 Hz), 6.05 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 13.83$, 22.37, 23.08, 24.97, 26.44, 29.42, 29.74, 31.32, 36.21, 39.38, 43.14, 172.44, 208.76. HRMS (FAB$^+$) *m/z* Calcd for $C_{13}H_{26}NO_2$: ([M + H]$^+$), 228.1963. Found: *m/z* 228.1945.

Oxidation of 11-Dodecen-2-ol. A 20-mL flask was charged with 3.3 mg (0.010 mmol) of $Na_2WO_4 \cdot 2H_2O$, 4.7 mg (0.010 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 850 mg (7.5 mmol) of aqueous 30% H_2O_2. After the biphasic mixture was vigorously stirred at room temperature for 10 min, 922 mg (5.00 mmol) of 11-dodecen-2-ol was added. This mixture was heated at 90 °C for 3 h with stirring at 1000 rpm. After cooling to room temperature, 196.0 mg (0.988 mmol) of tetradecane was added to the organic phase. The yields of 11-dodecen-2-one and 11,12-epoxydodecan-2-one were determined by GC analysis to be 97 and 0.4%, respectively. The GC data were corrected by integrating the response of each analyte against tetradecane. GC (column, DB-1701, 0.25 mm×30 m, J&W

Scientific); carrier gas, helium (1.2 kg cm^{-2}); column temp, 165 °C; injection temp, 280 °C; split ratio, 100 : 1; t_R of tetradecane, 3.8 min; t_R of 11-dodecen-2-one, 5.1 min; t_R of 11,12-epoxydodecan-2-one, 14.4 min.

11-Dodecen-2-one:[61] ^{1}H NMR (400 MHz, CDCl$_3$) δ = 1.24—1.40 (m, 10H), 1.50—1.60 (m, 2H), 2.00—2.07 (m, 2H), 2.13 (s, 3H), 2.41 (t, 2H, J = 7.3 Hz), 4.90—4.95 (m, 1H), 4.95—5.02 (m, 1H), 5.81 (tdd, 1H, J = 6.8, 10.3, 17.1 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ = 23.82, 28.86, 29.02, 29.13, 29.26, 29.31, 29.80, 33.75, 43.77, 114.10, 139.14, 209.28.

11,12-Epoxydodecan-2-one: ^{1}H NMR (400 MHz, CDCl$_3$) δ = 1.18—1.55 (m, 14H), 2.07 (s, 3H), 2.36 (t, 2H, J = 7.2 Hz), 2.40 (dd, 1H, J = 2.6, 4.4 Hz), 2.68 (dd, 1H, J = 4.4, 4.4 Hz), 2.81—2.86 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ = 23.67, 25.80, 28.97, 29.13, 29.19, 29.21, 29.69, 32.32, 43.60, 46.92, 52.19, 209.05. HRMS (FAB$^+$) *m*/*z* Calcd for $C_{12}H_{23}O_2$: ([M + H]$^+$), 199.1698. Found: *m*/*z* 199.1700.

5-Cyclohexadecenone.[62] A mixture of 6.6 mg (0.020 mmol) of $Na_2WO_4 \cdot 2H_2O$, 18.6 mg (0.040 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 10.2 g (15.0 mmol) of aqueous 5% H_2O_2 was vigorously stirred at room temperature for 10 min. Then, 2.39 g (10.0 mmol) of 5-cyclohexadecenol (a 2 : 1 mixture of the *E* and *Z* isomer as judged by the ^{13}C NMR shift of the olefinic carbons (CDCl$_3$), δ = 130.61 and 131.58 (*E*) and 129.53 and 130.28 (*Z*)) and 2 mL of toluene were added, and the mixture was heated at 110 °C for 10.5 h without stirring. The disappearance of the substrate (conversion) and the formation of 5-cyclohexadecenone (selectivity) were determined to be 100 and 98%, respectively, by ^{1}H NMR analysis of small aliquots of the organic phase. The organic phase was separated, washed with 3 mL of saturated aqueous $Na_2S_2O_3$, and chromatographed on silica gel (BW 820, 35 g; eluent, 10 : 1 hexane–ether) to give 2.34 g (99%) of 5-cyclohexadecenone (a 2 : 1 mixture of the *E* and *Z* isomer) as a colorless liquid. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 1.21—1.40 (m, 14H), 1.63—1.68 (m, 4H), 1.98—2.10 (m, 4H), 2.31—2.46 (m, 4H), 5.25—5.40 (m, 2H). *E* isomer: ^{13}C NMR (100 MHz, CDCl$_3$) δ = 22.49, 23.33, 25.74, 25.89, 26.67, 26.78, 27.03, 27.17, 28.43, 31.21, 32.00, 40.54, 42.15, 129.91, 132.18, 212.51. *Z* isomer: ^{13}C NMR (100 MHz, CDC$_3$) δ = 23.19, 23.91, 26.24, 26.34, 26.49, 26.56, 26.65, 26.84, 26.87, 27.26, 28.13, 41.40, 42.50, 129.91, 130.91, 212.21.

Reaction with stirring at 1000 rpm under otherwise identical conditions gave 5-cyclohexadecenone and 5,6-epoxycyclohexadecanone in 91 and 4% yields (92 : 8), respectively.

5,6-Epoxycyclohexadecanone: ^{1}H NMR (400 MHz, CDCl$_3$) δ = 1.19—1.96 (m, 22H), 2.32—2.57 (m, 4H), 2.60—2.68 (m, 1H), 2.86—2.94 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ = 20.14, 20.85, 23.34, 23.69, 24.02, 24.96, 26.10, 26.40, 26.48, 26.50, 26.75, 27.02, 27.07, 27.11, 27.11, 27.16, 27.24, 27.31, 30.68, 30.83, 31.42, 34.50, 41.23, 41.46, 41.61, 42.50, 56.78, 56.84, 58.39, 58.76, 211.16, 211.45. HRMS (FAB$^+$) *m*/*z* Calcd for $C_{16}H_{29}O_2$: ([M + H]$^+$), 253.2167. Found: *m*/*z* 253.2185.

Oxidation of 1-Dodecen-3-ol. A 20-mL flask was charged with 6.6 mg (0.020 mmol) of $Na_2WO_4 \cdot 2H_2O$, 9.3 mg (0.020 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 1.13 g (10.0 mmol) of aqueous 30% H_2O_2. The biphasic mixture was vigorously stirred at room temperature for 10 min. Then, 1.84 g (10.0 mmol) of 1-dodecen-3-ol was added, and the mixture was heated at 90 °C for 3 h with stirring at 1000 rpm. After cooling to room temperature, 357.5 mg (1.802 mmol) of tetradecane was added to the organic phase. The yields of 1-dodecen-3-one, 1,2-epoxydodecan-3-one, and 1,2-epoxydodecan-3-ol were determined by GC analysis to be 80, 4, and 14%, respectively. The GC data were corrected by integrating the response of each analyte against tetradecane. GC (column, DB-WAX, 0.25 mm × 15 m, J&W Scienfitic); carrier gas, helium (1.2 kg cm^{-2}); column temp, 160 °C; injection temp, 200 °C; split ratio, 100 : 1; t_R of tetradecane, 0.6 min; t_R of 1-dodecen-3-one, 1.1 min; t_R of 1,2-epoxydodecan-3-one, 3.0 min; t_R of 1,2-epoxydodecan-3-ol, 4.9 min.

1-Dodecen-3-one:[63] ^{1}H NMR (400 MHz, CDCl$_3$) δ = 0.88 (t, 3H, J = 6.8 Hz), 1.20—1.40 (m, 12H), 1.50—1.70 (m, 2H), 2.58 (t, 2H, J = 7.6 Hz), 5.81 (dd, 1H, J = 1.6, 10.8 Hz), 6.21 (dd, 1H, J = 1.6, 17.6 Hz), 6.35 (dd, 1H, J = 10.8, 17.6 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ = 14.07, 22.64, 24.03, 29.24, 29.25, 29.40, 29.41, 31.85, 39.85, 127.79, 136.60, 201.14.

1,2-Epoxydodecan-3-one: ^{1}H NMR (400 MHz, CDCl$_3$) δ = 0.88 (t, 3H, J = 6.3 Hz), 1.20—1.34 (m, 12H), 1.44—1.53 (m, 2H), 2.23—2.48 (m, 2H), 2.86 (dd, 1H, J = 2.4, 5.9 Hz), 2.98 (dd, 1H, J = 4.4, 5.9 Hz), 3.42 (dd, 1H, J = 2.4, 4.4 Hz). ^{13}C NMR (100 MHz, CDCl$_3$) δ = 14.05, 22.62, 23.06, 29.11, 29.20, 29.31, 29.35, 31.81, 36.55, 46.03, 53.35, 207.80. HRMS (FAB$^+$) *m*/*z* Calcd for $C_{12}H_{23}O_2$: ([M + H]$^+$), 199.1698. Found: *m*/*z* 199.1695.

1,2-Epoxydodecan-3-ol: This epoxide was obtained as a 6 : 4 mixture of diastereoisomers. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 0.88 (t, 3H, J = 6.8 Hz), 1.10—1.65 (m, 16H), 1.84—1.87 (m, 0.6H), 1.91—1.95 (m, 0.4H), 2.70—2.74 (m, 1H), 2.79—2.84 (m, 1H), 2.96—3.04 (m, 1H), 3.40—3.47 (m, 0.4H), 3.82—3.83 (m, 0.6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ = 14.07, 22.64, 25.68, 29.28, 29.50, 29.51, 29.57, 29.64, 31.85, 33.43, 34.39, 43.37, 45.15, 54.52, 55.38, 68.39, 71.67. HRMS (FAB$^+$) *m*/*z* Calcd for $C_{12}H_{25}O_2$: ([M + H]$^+$), 201.1855. Found: *m*/*z* 201.1841.

Oxidation of 2-Methyl-2-undecen-4-ol. A 20-mL flask was charged with 3.3 mg (0.010 mmol) of $Na_2WO_4 \cdot 2H_2O$, 9.4 mg (0.020 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 567 mg (5.00 mmol) of aqueous 30% H_2O_2. After the mixture was vigorously stirred at room temperature for 10 min, 920 mg (4.99 mmol) of 2-methyl-2-undecen-4-ol was added. This mixture was heated at 110 °C for 0.5 h with stirring at 1000 rpm. The organic phase was separated, washed with 2 mL of saturated aqueous $Na_2S_2O_3$, and chromatographed on silica gel (BW 300, 20 g; eluent, 2 : 1 hexane–ether) to give 1.00 g (100%) of 2-methyl-2,3-epoxyundecan-4-ol as a colorless liquid. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 0.89 (t, 3H, J = 6.8 Hz), 1.24—1.53 (m, 16H), 1.58—1.67 (m, 2H), 2.05—2.07 (m, 1H), 2.70 (d, 1H, J = 7.8 Hz), 3.45—3.50 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ = 14.06, 19.42, 22.62, 24.91, 24.96, 29.18, 29.60, 31.78, 34.00, 59.67, 67.83, 70.41. Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08%. Found: C, 71.65; H, 12.48%.

Octanoic Acid. The reaction was run in a manner identical with the procedure for Oxidation of 2-Octanol, except that 5.08 g (15.4 mmol) of $Na_2WO_4 \cdot 2H_2O$, 7.17 g (15.4 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 218 g (1.92 mol) of aqueous 30% H_2O_2 were used. Bp 93.0—95.0 °C/0.5 mmHg. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 0.88 (t, 3H, J = 6.8 Hz), 1.28—1.33 (m, 8H), 1.63 (tt, 2H, J = 7.3, 7.3 Hz), 2.35 (t, 2H, J = 7.3 Hz), 11.45 (br, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ = 14.02, 22.57, 24.66, 28.88, 29.00, 31.61, 34.09, 180.39. HRMS (EI$^+$) *m*/*z* Calcd for $C_8H_{16}O_2$: (M$^+$), 144.1150. Found: *m*/*z* 144.1130.

A 20-mL flask was charged with 132 mg (0.400 mmol) of $Na_2WO_4 \cdot 2H_2O$, 186 mg (0.400 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 5.69 g (50.0 mmol) of aqueous 30% H_2O_2. After the biphasic mixture was vigorously stirred at room temperature for 10 min, 2.60 g (20.0 mmol) of 1-octanol was added. This mixture was heated at 90 °C for 4 h with stirring at 1000 rpm. After cooling to room temperature, 805.1 mg (4.367 mmol) of tridecane was added to the organic phase. Octanoic acid was analyzed after conversion to the methyl ester by adding an excess amount of trimethylsilyldiazomethane to small aliquots of the organic phase. The yields of octanoic acid and octyl octanoate were determined by GC analysis to be 82 and 2%, respectively. The GC data were corrected by integrating the response of each analyte against tridecane. GC (column, OV-1, 0.25 mm×50 m, GL Sciences Inc.); carrier gas, helium (1.2 kg cm^{-2}); initial column temp, 80 °C; final column temp, 280 °C; progress rate, 15 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of methyl octanoate, 8.3 min; t_R of tridecane, 10.4 min; t_R of octyl octanoate, 15.6 min.

Octyl Octanoate: ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.88$ (t, 6H, $J = 6.8$ Hz), 1.28—1.30 (m, 18H), 1.60—1.63 (m, 4H), 2.29 (t, 2H, $J = 7.3$ Hz), 4.06 (t, 2H, $J = 6.3$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 14.01$, 14.04, 22.57, 22.61, 25.01, 25.92, 28.64, 28.91, 29.09, 29.16, 29.19, 31.65, 31.76, 34.39, 64.36, 173.98. HRMS (FAB$^+$) m/z Calcd for $C_{16}H_{33}O_2$: ([M + H]$^+$), 257.2481. Found: m/z 257.2478.

Nonanoic Acid. The reaction was run under conditions similar to the procedure for Oxidation of 2-Octanol, except that 4.59 g (13.9 mmol) of $Na_2WO_4{\cdot}2H_2O$, 6.47 g (13.9 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 197 g (1.73 mol) of aqueous 30% H_2O_2 were used. Bp 105.0—107.0 °C/0.5 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.88$ (t, 3H, $J = 6.8$ Hz), 1.28—1.33 (m, 10H), 1.60—1.67 (m, 2H), 2.34 (t, 2H, $J = 7.2$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 14.01$, 22.61, 24.65, 29.04, 29.07, 29.18, 31.78, 34.12, 180.51. HRMS (EI$^+$) m/z Calcd for $C_9H_{18}O_2$: (M$^+$), 158.1307. Found: m/z 158.1286.

2-Ethylhexanoic Acid. The reaction was performed under conditions similar to the procedure for Oxidation of 2-Octanol, except that 5.07 g (15.4 mmol) of $Na_2WO_4{\cdot}2H_2O$, 7.15 g (15.4 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 218 g (1.92 mol) of aqueous 30% H_2O_2 were used. Bp 105.0—110.0 °C/2 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.90$ (t, 3H, $J = 7.2$ Hz), 0.94 (t, 3H, $J = 7.2$ Hz), 1.27—1.34 (m, 4H), 1.44—1.69 (m, 4H), 2.28 (tt, 1H, $J = 5.2$, 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 11.72$, 13.88, 22.62, 25.15, 29.50, 31.44, 47.12, 183.16. HRMS (EI$^+$) m/z Calcd for $C_8H_{16}O_2$: (M$^+$), 144.1150. Found: m/z 144.1162.

2,2-Dimethylpropanoic Acid.[64] The reaction was run in a manner identical with the procedure for Oxidation of 2-Octanol using 7.48 g (22.7 mmol) of $Na_2WO_4{\cdot}2H_2O$, 10.6 g (22.7 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 322 g (2.84 mol) of aqueous 30% H_2O_2. Bp 72.0—75.0 °C/20 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.23$ (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 26.94$, 38.57, 185.52.

***p*-Methoxybenzoic Acid.** A 50-mL flask was charged with 99.0 mg (0.30 mmol) of $Na_2WO_4{\cdot}2H_2O$, 140 mg (0.30 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 2.04 g (3.0 mmol) of aqueous 5% H_2O_2. After the mixture was vigorously stirred at room temperature for 10 min, 4.15 g (30 mmol) of *p*-methoxybenzyl alcohol and 6 mL of toluene were added. This mixture was heated at 70 °C for 10 min with stirring at 1000 rpm, then 16.7 g (147 mmol) of aqueous 30% H_2O_2 was added dropwise using a syringe pump over a period of 12 h. The organic phase was separated, and the aqueous phase was extracted with 20 mL of ethyl acetate. The combined organic phases were extracted with saturated aqueous $NaHCO_3$ (2×20 mL). The $NaHCO_3$ solution and the aqueous phase were combined, acidified to pH 2 with concentrated HCl, and extracted with ethyl acetate (2×20 mL). The organic phase was concentrated and chromatographed on silica gel (BW 300, 30 g; eluent, 2 : 1 hexane–ether) to give 218 mg (5%) of *p*-methoxybenzoic acid as a pale yellow solid. Mp 187.0—190.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$–DMSO-d_6) $\delta = 3.78$ (s, 3H), 6.82 (d, 2H, $J = 7.5$ Hz), 7.86 (d, 2H, $J = 7.5$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$–DMSO-d_6) $\delta = 54.89$, 113.03, 122.82, 131.14, 162.58, 167.30. Anal. Calcd for $C_8H_8O_3$: C, 63.15; H, 5.30%. Found: C, 63.16; H, 5.22%. The remaining organic phase was washed with 20 mL of saturated aqueous $Na_2S_2O_3$, and chromatographed on silica gel (BW 300, 50 g; eluent, 5 : 1 hexane–ether) to afford 1.17 g (29%) of *p*-methoxybenzaldehyde as a colorless liquid.

***p*-Methybenzoic Acid.** A 1-L, three-necked flask equipped with a magnetic stirring bar, a reflux condenser, and a 100-mL dropping funnel was charged with 2.70 g (8.19 mmol) of $Na_2WO_4{\cdot}2H_2O$, 3.81 g (8.19 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 55.8 g (81.9 mmol) of aqueous 5% H_2O_2. After the mixture was vigorously stirred at room temperature for 10 min, 100 g (819 mmol) of *p*-methylbenzyl alcohol was added. This mixture was heated at 90 °C with stirring at 1000 rpm, then 455 g (4.01 mol) of aqueous 30% H_2O_2 was added dropwise via the dropping funnel over a period of 12 h. The resulting precipitate was separated by filtration, dissolved in 500 mL of ethyl acetate and washed with 100 mL of saturated aqueous $Na_2S_2O_3$. The organic phase was separated and concentrated under reduced pressure. The product was recrystallized from 4 : 1 methanol–water giving 88.8 g (80%) of *p*-methylbenzoic acid as pale yellow crystals. Mp 178.0—179.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 2.43$ (s, 3H), 7.27 (d, 2H, $J = 8.0$ Hz), 8.01 (d, 2H, $J = 8.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 21.74$, 126.65, 129.19, 130.25, 144.61, 172.40. Anal. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92%. Found: C, 70.28; H, 5.75%.

Benzoic Acid.[65] A mixture of 3.05 g (9.25 mmol) of $Na_2WO_4{\cdot}2H_2O$, 4.31 g (9.25 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 63.0 g (92.5 mmol) of aqueous 5% H_2O_2 was vigorously stirred at room temperature for 10 min. Then, 100 g (925 mmol) of benzyl alcohol was added, and the mixture was heated at 90 °C. With stirring at 1000 rpm, 252 g (2.22 mol) of aqueous 30% H_2O_2 was added dropwise over a period of 5 h. The resulting precipitate was separated by filtration, dissolved in 200 mL of ethyl acetate and washed with 100 mL of saturated aqueous $Na_2S_2O_3$. The organic phase was separated and concentrated under reduced pressure. The product was recrystallized from 4 : 1 methanol–water giving 91.0 g (81%) of benzoic acid as white crystals. Mp 120.0—121.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.47$ (t, 2H, $J = 7.3$ Hz), 7.61 (tt, 1H, $J = 1.5$, 7.3 Hz), 8.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 128.46$, 129.42, 130.20, 133.75, 172.31.

***p*-Bromobenzoic Acid.** The reaction was run under conditions similar to the procedure for Oxidation of 2-Octanol using 1.76 g (5.35 mmol) of $Na_2WO_4{\cdot}2H_2O$, 2.49 g (5.35 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 243 g (2.14 mol) of aqueous 30% H_2O_2. The solid product was dissolved in 500 mL of ethyl acetate, washed with 100 mL of saturated aqueous $Na_2S_2O_3$, and recrystallized from 4 : 1 methanol–water to give 92.0 g (86%) of *p*-bromobenzoic acid as pale yellow crystals. Mp 250.0—251.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$–DMSO-d_6) $\delta = 7.62$ (d, 2H, $J = 8.5$ Hz), 7.88 (d, 2H, $J = 8.5$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$–DMSO-d_6) $\delta = 125.29$, 128.39, 129.50, 129.74, 165.05. Anal. Calcd for $C_7H_5BrO_2$: C, 41.82; H, 2.51%. Found: C, 42.01; H, 2.28%.

***p*-Chlorobenzoic Acid.** The reaction was run in a manner identical with the procedure for Oxidation of 2-Octanol using 2.31 g (7.01 mmol) of $Na_2WO_4{\cdot}2H_2O$, 3.27 g (7.01 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 318 g (2.81 mol) of aqueous 30% H_2O_2. The solid product was dissolved in 500 mL of ethyl acetate, washed with 100 mL of saturated aqueous $Na_2S_2O_3$, and recrystallized from 4 : 1 methanol–water to give 95.1 g (87%) of *p*-chlorobenzoic acid as pale yellow crystals. Mp 237.0—239.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$–DMSO-d_6) $\delta = 7.44$ (d, 2H, $J = 8.5$ Hz), 7.95 (d, 2H, $J = 8.5$

Hz). ^{13}C NMR (100 MHz, $CDCl_3$–DMSO-d_6) δ = 126.88, 128.23, 129.50, 136.66, 165.26. Anal. Calcd for $C_7H_5ClO_2$: C, 53.70; H, 3.22%. Found: C, 53.63; H, 3.18%.

***p*-Nitrobenzoic Acid.** The reaction was performed under conditions similar to the procedure for Oxidation of 2-Octanol using 2.15 g (6.53 mmol) of $Na_2WO_4 \cdot 2H_2O$, 3.04 g (6.53 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 296 g (2.61 mol) of aqueous 30% H_2O_2. The solid product was dissolved in 500 mL of ethyl acetate, washed with 100 mL of saturated aqueous $Na_2S_2O_3$, and recrystallized from 4 : 1 methanol–water to give 99.6 g (91%) of *p*-nitrobenzoic acid as pale yellow crystals. Mp 238.0—239.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$–DMSO-d_6) δ = 8.19 (d, 2H, J = 8.4 Hz), 8.28 (d, 2H, J = 8.4 Hz), 10.17 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$–DMSO-d_6) δ = 121.81, 129.13, 135.18, 148.50, 164.38. Anal. Calcd for $C_7H_5NO_4$: C, 50.31; H, 3.02; N, 8.38%. Found: C, 50.48; H, 2.98; N, 8.27%. The yield determined by HPLC was 97%. HPLC (column, Develosil ODS-5, 4.6 mm×25 cm, Nomura Chemical); eluent, 55 : 45 water–acetonitrile mixture (contains 0.05% of TFA); flow rate, 1.0 mL min^{-1}; detection, 254-nm light; t_R of *p*-nitrobenzoic acid, 6.8 min; t_R of nitrobenzene (internal standard), 13.7 min. The solid product prior to the treatment with aqueous $Na_2S_2O_3$ was contaminated with 5% of the perbenzoic acid.

***p*-Methoxybenzaldehyde.** The reaction was performed in a manner identical with the procedure for Oxidation of Benzyl Alcohol to Benzaldehyde, except that 4.77 g (14.5 mmol) of $Na_2WO_4 \cdot 2H_2O$, 6.79 g (14.5 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, 49.3 g (72.4 mmol) of aqueous 5% H_2O_2, 114 g (1.01 mol) of aqueous 30% H_2O_2, and 150 mL of toluene were used at 70 °C for 5 h. Bp 137.0—138.0 °C/23 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.89 (s, 3H), 7.01 (d, 2H, J = 8.8 Hz), 7.84 (d, 2H, J = 8.8 Hz), 9.89 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 55.55, 114.28, 129.94, 131.95, 164.58, 190.76. HRMS (EI$^+$) m/z Calcd for $C_8H_8O_2$: (M$^+$), 136.0524. Found: m/z 136.0515.

***p*-Methybenzaldehyde.** The reaction was run for 4.5 h under conditions similar to the procedure for Oxidation of Benzyl Alcohol to Benzaldehyde using 1.35 g (4.09 mmol) of $Na_2WO_4 \cdot 2H_2O$, 1.91 g (4.09 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, 55.6 g (81.8 mmol) of aqueous 5% H_2O_2, and 92.8 g (819 mmol) of aqueous 30% H_2O_2. Bp 104.0—106.0 °C/30 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.44 (s, 3H), 7.33 (d, 2H, J = 8.0 Hz), 7.78 (d, 2H, J = 8.0 Hz), 9.96 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.85, 129.68, 129.82, 134.19, 145.51, 191.95. HRMS (EI$^+$) m/z Calcd for C_8H_8O: (M$^+$), 120.0575. Found: m/z 120.0556.

***o*-Methybenzaldehyde.** The reaction was run for 4.5 h under conditions similar to the procedure for Oxidation of Benzyl Alcohol to Benzaldehyde using 1.35 g (4.09 mmol) of $Na_2WO_4 \cdot 2H_2O$, 1.91 g (4.09 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, 55.6 g (81.8 mmol) of aqueous 5% H_2O_2, and 92.8 g (819 mmol) of aqueous 30% H_2O_2. Bp 87.0—89.0 °C/23 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.68 (s, 3H), 7.26 (d, 2H, J = 7.8 Hz), 7.36 (dd, 2H, J = 7.3, 7.8 Hz), 7.48 (ddd, 2H, J = 1.5, 7.3, 7.8 Hz), 7.80 (dd, 2H, J = 1.5, 7.8 Hz), 10.28 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 19.56, 126.30, 131.75, 132.03, 133.62, 134.14, 140.60, 192.78. HRMS (EI$^+$) m/z Calcd for C_8H_8O: (M$^+$), 120.0575. Found: m/z 120.0555.

Benzaldehyde.[66] Bp 81.0—82.0 °C/28 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53 (dd, 2H, J = 7.5, 7.8 Hz), 7.63 (dt, 1H, J = 1.5, 7.5 Hz), 7.88 (dd, 2H, J = 1.5, 7.8 Hz), 10.03 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 128.98, 129.73, 134.44, 136.41, 192.35.

***p*-Bromobenzaldehyde.** The reaction was run for 4.5 h in a manner identical with the procedure for Oxidation of Benzyl Alcohol to Benzaldehyde using 882 mg (2.67 mmol) of $Na_2WO_4 \cdot 2H_2O$, 1.25 g (2.67 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, 36.4 g (53.5 mmol) of aqueous 5% H_2O_2, and 72.8 g (642 mmol) of aqueous 30% H_2O_2. Bp 123.0—125.0 °C/23 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (d, 2H, J = 8.3 Hz), 7.75 (d, 2H, J = 8.3 Hz), 9.98 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 129.76, 130.95, 132.42, 135.05, 191.03. Anal. Calcd for C_7H_5BrO: C, 45.44; H, 2.72%. Found: C, 45.14; H, 2.55%.

***p*-Chlorobenzaldehyde.** The reaction was run for 4 h under conditions similar to the procedure for Oxidation of Benzyl Alcohol to Benzaldehyde using 1.16 g (3.51 mmol) of $Na_2WO_4 \cdot 2H_2O$, 1.63 g (3.51 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, 47.6 g (70.0 mmol) of aqueous 5% H_2O_2, and 87.3 g (770 mmol) of aqueous 30% H_2O_2. Bp 120.0—125.0 °C/45—50 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (d, 2H, J = 8.3 Hz), 7.79 (d, 2H, J = 8.3 Hz), 9.95 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 129.36, 130.82, 134.64, 140.84, 190.75. Anal. Calcd for C_7H_5ClO: C, 59.81; H, 3.59%. Found: C, 59.48; H, 3.57%.

***p*-Nitrobenzaldehyde.** A 20-mL flask was charged with 33.0 mg (0.10 mmol) of $Na_2WO_4 \cdot 2H_2O$, 23.3 mg (0.05 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 136 mg (0.2 mmol) of aqueous 5% H_2O_2. After the mixture was vigorously stirred at room temperature for 10 min, 763 mg (4.98 mmol) of *p*-nitrobenzyl alcohol, 8 mL of toluene, and 2 mL of ethyl acetate were added. With stirring at 1000 rpm at 90 °C, 6.66 g (9.8 mmol) of aqueous 5% H_2O_2 was added dropwise using a syringe pump over a period of 17 h. The yield and conversion were determined to be 59 and 80%, respectively, by HPLC analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09 (d, 2H, J = 8.8 Hz), 8.41 (d, 2H, J = 8.8 Hz), 10.17 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 124.26, 130.44, 140.01, 151.08, 190.25. Anal. Calcd for $C_7H_5NO_3$: C, 55.63; H, 3.33; N, 9.27%. Found: C, 55.79; H, 3.18; N, 9.14%. HPLC (column, Develosil ODS-5, 4.6 mm×25 cm, Nomura Chemical); eluent, 55 : 45 water–acetonitrile mixture (contains 0.05% of TFA); flow rate, 1.0 mL min^{-1}; detection, 254-nm light; t_R of *p*-nitrobenzoic acid, 6.8 min; t_R of *p*-nitrobenzaldehyde, 9.6 min; t_R of nitrobenzene (internal standard), 13.7 min.

2- Naphthalenecarbaldehyde. A mixture of 1.04 g (3.20 mmol) of $Na_2WO_4 \cdot 2H_2O$, 1.47 g (3.20 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, 516 g (759 mmol) of aqueous 5% H_2O_2 was vigorously stirred at room temperature for 10 min. Then 100 g (632 mmol) of 2-napthalenemethanol was added, and the mixture was heated at 90 °C for 4.5 h with stirring at 1000 rpm. The resulting precipitate was separated by filtration, washed with 50 mL of saturated aqueous $Na_2S_2O_3$, and distilled through a short column to give 81.3 g (82%) of 2-naphthalenecarbaldehyde as a pale yellow solid. Bp 139.0—141.0 °C/3.5—4 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (ddd, 1H, J = 1.5, 6.8, 8.0 Hz), 7.63 (ddd, 1H, J = 1.5, 6.8, 7.6 Hz), 7.88—7.99 (m, 4H), 8.31 (s, 1H), 10.14 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 122.70, 127.03, 128.02, 129.03, 129.05, 129.47, 132.58, 134.05, 134.48, 136.39, 192.17. Anal. Calcd for $C_{11}H_8O$: C, 84.59; H, 5.16%. Found: C, 84.31; H, 5.21%.

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