General Oxygenation Procedure. An apparently heterogeneous mixture of an olefin (cyclohexene, 1-pentene, or styrene, 1 g), $NaBH_4$ (300 mg, 7.9 mmol), (OEP)$Rh^{III}Cl$ (4.0 mg, 6 μmol; [Rh] = 0.6 mM), and an internal standard (*p*-xylene, mesitylene, or durene, appropriate amount) in dry THF (10 mL) exposed to dry air was stirred at 20–25 °C. The oxygenation of 1-methylcyclohexene was carried out by using the rhodium catalyst in an amount 2 or 20 times as much as that used above ([Rh] = 1.2 or 12 mM). The electronic spectra of the reaction mixture underwent no significant change even after 100 h. The formation of oxygenation products was monitored by gas chromatography. Similarly was carried out the oxygenation of 1,5-cyclooctadiene and acetylenes (1-heptyne and 3-heptyne) by using substrate (300 mg), $NaBH_4$ (300 mg), and (OEP)$Rh^{III}Cl$ or (TPP)$Rh^{III}Cl$ (4.0 mg) in THF (20 mL). Reaction products, after conversion if necessary to silylated derivatives, were identified by gas chromatography on the basis of coinjection with authentic samples, and their yields determined also by gas chromatography. 2-Methylcyclohexanol as a mixture of stereoisomers arising from the oxygenation of 1-methylcyclohexene was purified by preparative gas chromatography. The stereoisomer distribution was determined by ^1H NMR spectroscopy by taking advantage of the characteristic signals for hydroxymethine protons at δ 3.1 (for *E* isomer) and 3.75 (for *Z* isomer).

The following control runs were carried out by using cyclohexene as substrate: (1) without rhodium porphyrin catalyst, (2) without O_2, (3) without $NaBH_4$, and (4) with $NaBH(OCH_3)_3$ in place of $NaBH_4$. In neither case was detected oxygenation of substrate to any significant extent. Another control run using cyclohexene oxide in place of cyclohexene under otherwise identical oxygenation conditions did not give cyclohexanol.

Borane Transfer. A mixture of (OEP)$Rh^{III}Cl$ (40 mg, 0.06 mmol), $NaBH_4$ (100 mg, 2.64 mmol), and 1-pentene (70 mg, 1.0 mmol) in THF (2 mL) in a vessel sealed with a rubber septum was degassed by freeze–pump–thaw cycles and was stirred at room temperature for 19 h. The electronic spectrum of the mixture showed λ_{max} at 395, 514, and 545 nm, indicating the formation of (OEP)RhH.[3] Following the standard procedure for the analysis of organoboranes,[28] the mixture was then subjected to gas chromatography at 170 °C on a column of silicone SE-30 (2 m), which had been treated with Silyl-8 (Pierce Chemical Co.) to mask protic sites with trimethylsilyl groups. The product was readily identified as tripentylborane on the basis of coinjection with the authentic sample prepared by hydroboration of olefin with diborane under standard conditions. The mixture was exposed to air, stirred for 20 min, and then analyzed by gas chromatography to show the formation of 1-pentanol and 2-pentanol (94:6, in a total yield of 45% based on mol of Rh complex used).

Oxidation of Alkylborane. A THF solution of (*E*)-bis(2-methylcyclohexyl)borane[11] was prepared by the hydroboration of 1-methylcyclohexene (96 mg, 1.0 mmol) with borane–THF (1 M) (0.5 mL, 0.5 mmol) in THF (1 mL) under nitrogen. To this was added 1 N aqueous NaOH (0.5 mL), and the mixture was stirred under air atmosphere for 20 h. Gas chromatographic analysis using silicone DCQF-1 showed the formation of 2-methylcyclohexanol with the stereoisomer ratio of *E*/*Z* = 76:24. Another control run for the oxidation of alkylborane with O_2 was carried out in the presence of $NaBH_4$ (38 mg, 1.0 mmol) instead of aqueous NaOH under otherwise identical conditions and gave the isomer ratio of *E*/*Z* = 81:19.

A solution of (*E*)-bis(2-methylcyclohexyl)borane in THF (0.21 mL) was prepared as above starting from the olefin (15.4 mg, 0.16 mmol). This solution was added to (OEP)RhH[15] (100 mg, 0.16 mmol) under nitrogen. The mixture was then allowed to contact with a gentle stream of THF-saturated air for 20 h. Gas chromatography coupled with ^1H NMR analysis indicated almost exclusive formation of (*E*)-2-methylcyclohexanol.

(28) Reference 4b, pp 246–248.

Fast and Selective Oxidation of Primary Alcohols to Aldehydes or to Carboxylic Acids and of Secondary Alcohols to Ketones Mediated by Oxoammonium Salts under Two-Phase Conditions

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Primary alcohols are quantitatively oxidized to aldehydes in a few minutes at 0 °C in CH_2Cl_2–0.35 M aqueous NaOCl in the presence of catalytic amounts of 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (**3b**). Cocatalysis by Br^- and buffering of pH at 8.6 with $NaHCO_3$ are also required. Secondary alcohols are converted to ketones. Further oxidation of aldehydes to carboxylic acids is slow, but the reaction is completed in a few minutes under the same conditions by addition of catalytic amounts of phase-transfer catalyst. All reactions are highly selective. Only a slight excess of NaOCl is required. The method can be applied to saturated alkyl and aryl alkyl substrates.

Selective oxidation of primary alcohols to aldehydes is one of the long standing problems of organic chemistry. Although a huge number of methods of oxidation is known,[1] it is difficult to find a procedure which is selective, cheap, efficient, and easy to work up.

Oxoammonium salts 1 oxidize primary and secondary alcohols to the corresponding carbonyl derivatives.[2] Both stoichiometric[3] and catalytic procedures have been described. Catalytic cycles include electrooxidation,[4] and oxidations by $CuCl_2$–O_2[5] or by peroxy acids.[6] It has been

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(2) Rozantsev, E. G.; Sholle, V. D. *Synthesis* **1971**, 401.

(3) (a) Golubev, V. A.; Rozantsev, E. G.; Neiman, M. B. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1965**, 1927; *Chem. Abstr.* **1966**, *64*, 11164e. (b) Ganem, B. *J. Org. Chem.* **1975**, *40*, 1998. (c) Miyazawa, T.; Endo, T.; Siihashi, S.; Okawara, M. *J. Org. Chem.* **1985**, *50*, 1332. (d) Miyazawa, T.; Endo, T. *J. Org. Chem.* **1985**, *50*, 3930.
(4) Semmelhack, M. F.; Chou, C. S.; Cortês, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 4492.
(5) Semmelhack, M. F.; Schmid, C. R.; Cortês, D. A.; Chou, C. S. *J. Am. Chem. Soc.* **1984**, *106*, 3374.

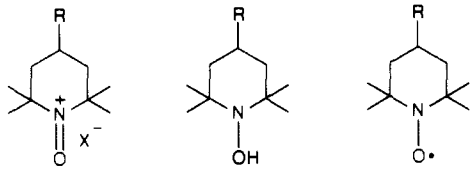
0022-3263/87/1952-2559$01.50/0

Table I. Oxidation of Primary and Secondary Alcohols to Carbonyl Derivatives[a]

entry	alcohol	time, min	yield, %[b,c]
1	1-pentanol	3	99
2	1-heptanol	3	98
3	1-nonanol	3	98 (92)
4	1-nonanol	3	98[d]
5	1-undecanol	3	98 (93)
6	$\overline{OC(CH_3)_2OCH_2}CH(CH_2)_3CH_2OH$	3	96
7	benzyl alcohol	3	95 (90)
8	*m*-nitrobenzyl alcohol	3	100
9	*p*-nitrobenzyl alcohol	3	100
10	*p*-methoxybenzyl alcohol	45	30[e]
11	*p*-methoxybenzyl alcohol	2	98[f]
12	cinnamyl alcohol	30	20[g]
13	2-octanol	10	99 (80)[h]
14	2-nonanol	10	98
15	cyclohexanol	7	98

[a] In CH_2Cl–H_2O at pH 8.6 and 0 °C with 0.01 mol equiv of **3b**, 0.10 mol equiv of KBr, and 1.25 mol equiv of 0.35 M aqueous NaOCl. [b] Conversions reached 100% if not otherwise indicated. [c] GLC values; isolated yields in parentheses. [d] Oxoammonium salt **1b**, X = Br (0.01 mol equiv), was used instead of **3b**. [e] Conversion was 62%. [f] In the presence of 0.05 mol equiv of Aliquat 336. [g] Conversion was 79%. In the presence of 0.05 mol equiv of Aliquat 336, 93% conversion and 57% yield were reached after 30 min. [h] Due to its high volatility, 2-octanone was lost in part during workup.

proposed[4,5] that oxoammonium salts **1** react with alcohols forming the carbonyl derivatives and hydroxylamines **2**: syn proportionation between **1** and **2** affords two molecules of nitroxyl **3**, which is oxidized again to 1.



1 **2** **3**

a, R = H
b, R = OCH_3

In this paper we describe an easy oxidation of primary alcohols to aldehydes or to carboxylic acids, in the presence of catalytic amounts of 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl **3b**, with continuous generation of oxoammonium salt **1b** by NaOCl under aqueous organic two-phase conditions. In these same conditions secondary alcohols are oxidized to ketones. Reactions are highly selective and are completed in a few minutes at 0 °C.[7]

Results and Discussion

The oxidation of alcohols to carbonyl derivatives was carried out at 0 °C in CH_2Cl_2–0.35 M aqueous NaOCl (1.25 mol equiv), in the presence of 0.01 mol equiv of nitroxyl radical **3b**. The addition of 0.10 mol equiv of KBr and buffering of the aqueous solution at pH 8.6 with $NaHCO_3$ were also required (eq 1). Under these conditions primary

$$RCH_2OH + NaOCl \xrightarrow[\textbf{3b}\ (0.01\ \text{mol equiv}),\ 0\ ^\circ C]{CH_2Cl_2\text{–}H_2O,\ NaHCO_3,\ KBr\ (0.1\ \text{mol equiv})} RCHO \quad (1)$$

aliphatic alcohols were quantitatively oxidized to aldehydes

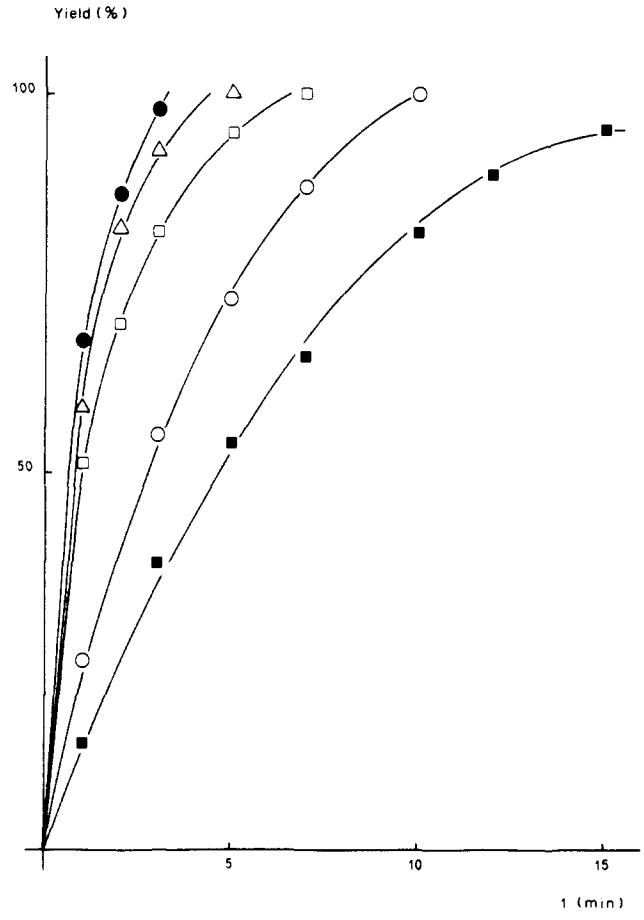


Figure 1. Oxidation of 1-nonanol to nonanal in CH_2Cl_2–H_2O with sodium hypochlorite (1.25 mol equiv) at pH 8.6 and 0 °C: 0.05 mol equiv of **3b** (○); 0.02 mol equiv of **3b** (■); 0.02 mol equiv of **3b** and 0.05 mol equiv of KBr (△); 0.01 mol equiv of **3b** and 0.10 mol equiv of KBr (●); 0.005 mol equiv of **3b** and 0.10 mol equiv of KBr (□).

within 3 min,[8] whereas the oxidation of secondary alcohols to ketones required 7–10 min (Table I). This difference of reaction rate is better evidenced by the competitive oxidation of a 1:1 mixture of 1-nonanol and 2-nonanol which afforded a 9:1 ratio of nonanal and 2-nonanone.[9]

The oxidation of alcohols to aldehydes or ketones can be applied to saturated alkyl and aryl alkyl substrates. Selectivities are always higher than 95%. Identical results are obtained when oxoammonium salt **1b** (X = Br) is used instead of **3b**: an example is reported in Table I (entry 4).

Relatively unstable protecting groups are not affected, as in the oxidation of the acetonide of 1,2,6-hexanetriol (entry 6). On the contrary, selectivity is fair for unsaturated alcohols, e.g., cinnamyl alcohol (entry 12), due to the competitive addition of hypohalogenous acids to the double bond.[10]

Benzyl alcohol is rapidly oxidized to benzaldehyde. The presence of electron-withdrawing groups in the aromatic ring has little influence on the oxidation rates but these are markedly lowered by introducing electron donor groups. Thus, benzyl alcohol and *p*-nitro and *m*-nitrobenzyl alcohols are quantitatively oxidized to aldehydes

(6) (a) Cella, J. A.; Kelley, J. A.; Kenehan, E. F. *J. Org. Chem.* **1975**, *40*, 1860. (b) Cella, J. A.; McGrath, J. P.; Kelley, J. A.; El Soukkary, O.; Hilpert, L. *J. Org. Chem.* **1977**, *42*, 2077.

(7) In the catalytic cycles realized in homogeneous phase[4-6] oxidations require on the average few hours at room temperature in the presence of 0.05–0.3 molar equiv of the catalyst.

(8) Low selectivities in the oxidation of primary aliphatic alcohols to aldehydes have been observed in stoichiometric[3b] and catalytic[5,6a] reactions carried out in homogeneous conditions.

(9) Preliminary oxidation tests of substrates containing both primary and secondary hydroxyls failed due to the high hydrophilicity of these compounds.

(10) Dalcanale, E.; Montanari, F. *J. Org. Chem.* **1986**, *51*, 567.

Table II. Oxidation of Alcohols to Carbonyl Derivatives. Influence of Temperature, pH, and Catalytic Species[a]

entry	alcohol	T, °C	pH	3b, mol equiv	KBr, mol equiv	Aliquat 336, mol equiv	time, min	yield,[b] %
1	1-nonanol	0	12.7	0.01	0.10		60	23
2	1-nonanol	0	8.6	0.01	0.10		3	98
3	1-nonanol	25	8.6	0.02			15	98
4	1-nonanol	25	8.6	0.02	0.05		15	77
5	1-nonanol	25	8.6	0.02	0.10		15	62
6	1-nonanol	25	12.7			0.05	60	4
7	1-nonanol	0	12.7			0.05	60	2
8	1-nonanol	25	12.7				60	1

[a] In CH_2Cl_2–H_2O with 1.25 mol equiv of 0.35 M aqueous NaOCl. [b] Selectivities were always ≥98%.

Table III. Amount of Oxidant[15] in the Organic Phase[a]

T, °C	time, s	oxidant,[b] mol equiv × 10^2
0	60	22.8
0	300	21.2
25	10	15.2
25	60	7.2
25	300	2.6
25	60	2.4[c]
25	300	2.4[c]

[a] After equilibration of 10 mL of a 0.008 M CH_2Cl_2 solution of **3b** with 14.3 mL of 0.35 M aqueous NaOCl at pH 8.6 containing 0.20 mmol of KBr. [b] Values are the average of four measurements. [c] After equilibration of 10 mL of CH_2Cl_2 with 14.3 mL of 0.35 M aqueous NaOCl at pH 8.6 containing 0.20 mmol of KBr.

in 3 min under standard conditions (entries 7–9), but conversion of *p*-methoxybenzyl alcohol is still incomplete (62%) after 45 min (entry 10). In this case the slow oxidation to aldehyde is accompanied by the formation of unidentified side products. The problem was solved by addition of 0.05 mol equiv of a quaternary salt (entry 11), thus obtaining 98% of the aldehyde in 2 min at 0 °C.

At the pH of commercial bleach (12.7) reactions are very slow (Table II, entry 1), and the pH must be lowered in order to speed up the rate. Indeed, at pH 8.6 hypochlorous acid is distributed between the aqueous and the organic phase.[11] This makes the addition of a phase-transfer catalyst not necessary, unless the presence of strongly basic ClO^- and BrO^- anions in the organic phase is required (see later).

At pH 8.6 and 0 °C, 95% of 1-nonanol is converted to nonanal in 15 min by using 0.02 mol equiv of nitroxyl **3b** (Figure 1). By adding 0.05 mol equiv of KBr the same conversion is reached in 3–5 min; this is most likely due to the formation of the more powerful oxidant HOBr.[12] It is possible to decrease the amount of one catalytic species (**3b** or KBr) if the other is increased, thus allowing fast reactions even with 0.005 mol equiv of **3b**.

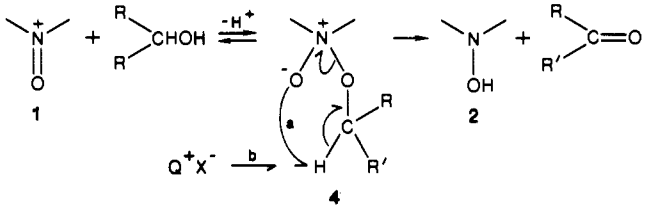
Paradoxically, oxidations are slowed down by increasing the temperature and, at 25 °C, the addition of KBr has an inhibitor effect (Table II, entries 3–5). Indeed, oxoammonium salts are highly unstable species:[2,13] they produce hydrogen peroxide in aqueous solutions of alkali hydroxides[14] and are even slowly reduced by water.[3a,14a] As shown in Table III, their stability under the reaction conditions strongly depends on the temperature: at 25 °C, in the absence of a substrate, the amount of the oxidant

Table IV. Oxidation of Primary Alcohols and Aldehydes to Carboxylic Acids[a]

entry	substrate	NaOCl, mol equiv	time, min	yield, %[b]
1	1-heptanol	2.5	5	99 (96)
2	heptanal	1.25	5	96
3	1-nonanol	2.5	5	98
4	nonanal	1.25	5	98
5	1-undecanol	2.5	5	98
6	undecanal	1.25	5	98
7	*m*-nitrobenzyl alcohol	2.5	5	(88)
8	*m*-nitrobenzaldehyde	1.25	5	(87)
9	*p*-methoxybenzyl alcohol	2.5	30	(5)[c]
10	*p*-methoxybenzaldehyde	1.25	30	(13)
11	1-nonanol	2.5	60	50[d]
12	nonanal	1.25	60	40[e]

[a] In CH_2Cl_2–H_2O at pH 8.6 and 0 °C with 0.01 mol equiv of **3b**, 0.10 mol equiv of KBr, and 0.05 mol equiv of Aliquat 336. [b] GLC yields, after acidification of the reaction mixture; isolated yields in parentheses. [c] The main product (90%) was *p*-methoxybenzaldehyde. [d] In the absence of Aliquat 336. [e] In the absence of **3b** and KBr.

Scheme I



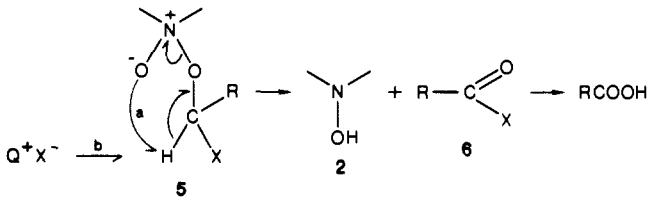
in the organic phase[15] rapidly diminishes; at 0 °C it remains practically constant. Under the same conditions, but in the absence of **3b**, HOCl and HOBr dissolved in CH_2Cl_2 are stable (up to 300 s) even at 25 °C.

The presence of oxoammonium salt **1b**, or of its precursor **3b**, is essential. Although oxidation of alcohols with NaOCl under phase-transfer conditions have already been described,[16] they are much slower (and less selective)[16] than those described in the present paper. For example extremely low conversions of 1-nonanol to nonanal are obtained by using 0.05 mol equiv of methyltrioctylammonium chloride (Aliquat 336) and 1.25 mol equiv of 0.35 M aqueous NaOCl at 0 and 25 °C and without any oxoammonium catalyst at 25 °C (Table II, entries 6–8).

Under standard conditions the oxidation of aldehydes to carboxylic acids is slow even in the presence of an excess of NaOCl. However, the reactions are completed in 5 min

(11) Montanari, F.; Penso, M.; Quici, S.; Viganò, P. *J. Org. Chem.* **1985**, *50*, 4888.
(12) *Encyclopedia of Chemical Technology* (*Kirk-Othmer*), 3rd ed.; Wiley: New York, 1978; Vol. 3, p 769.
(13) Dagonneau, M.; Kagan, E. S.; Mikhailov, V. I.; Rozantsev, E. G.; Sholle, V. D. *Synthesis* **1984**, 895 and references therein.
(14) (a) Osiecki, J. H.; Ullman, E. F. *J. Am. Chem. Soc.* **1968**, *90*, 1078. (b) Endo, T.; Miyazawa, T.; Shiikashi, S.; Okawara, M. *J. Am. Chem. Soc.* **1984**, *106*, 3877.
(15) Apart oxoammonium cation **3b**, the other oxidizing species present in the organic phase are likely ClO^- and BrO^- associated with **3b**, HOCl[11] and HOBr.
(16) (a) Lee, G. A.; Freedman, H. H. *Tetrahedron Lett.* **1976**, 1641. (b) Lee, G. A.; Freedman, H. H. *Isr. J. Chem.* **1985**, *26*, 229 and references therein. (c) Abramovici, S.; Neumann, R.; Sasson, Y. *J. Mol. Catal.* **1985**, *29*, 291, (d) 299.

Scheme II



at 0 °C when catalytic amounts of a quaternary ammonium salt are added (eq 2, Table IV).

$$RCH_2OH + NaOCl \xrightarrow[\text{3b (0.01 mol equiv), } Q^+X^- \text{ (0.05 mol equiv), 0 °C}]{CH_2Cl_2\text{–}H_2O,\ NaHCO_3,\ KBr\ (0.1\ mol\ equiv)} RCOOH \quad (2)$$

Selectivity is >95%, and only a slight excess of oxidant is needed (1.25 and 2.50 mol equiv from aldehydes and from primary alcohols, respectively). In the presence of a quaternary salt, but in the absence of **3b**, oxidation of aldehydes to carboxylic acids is again very slow (entry 12). As expected, the electronic effects of substituents are equally important in the conversion of aldehydes to carboxylic acids, since, in contrast with *m*-nitrobenzaldehyde, *p*-methoxybenzaldehyde is oxidized very slowly (entries 8, 10).

According to the proposals made by other authors[3a,b,17] for oxidations mediated by oxoammonium salts under homogeneous conditions, it is possible that in the oxidation of alcohols to carbonyl derivatives under two-phase conditions an intermediate adduct **4** is formed at the equilibrium (Scheme I). Subsequent proton abstraction to give the carbonyl derivative and the hydroxylamine **2** might occur. The relevant electronic effects are in agreement with the development of a negative charge in the rate-determining step:[18] proton abstraction may occur intramolecularly (path a) or intermolecularly (path b) when a phase-transfer catalyst is needed.[19]

A similar mechanism is tentatively proposed (Scheme II) for the oxidation of aldehydes to carboxylic acids:[22] successive equilibria can lead to the intermediate adduct **5**, followed by intramolecular (path a) or intermolecular (path b) deprotonation in the rate-determining step.

In conclusion, the catalytic process of oxidation reported here allows a fast, selective, and high-yielding oxidation of saturated aliphatic and alkyl aromatic alcohols to aldehydes, ketones, or carboxylic acids. These processes appear to be much faster and easier then most reactions reported to date.[1] Furthermore, sodium hypochlorite is used in only slight excess and is rapidly and entirely consumed, an unusual behavior for reactions carried out under aqueous organic two-phase conditions.[20]

Experimental Section

General Methods. Reaction flasks were thermostated at the correct temperature within ±0.2 °C with circulating ethanol by a Colora Misstechnik GMBH Lorch/Württ. cryostat. Stirring speed was maintained at 1300 ± 50 rpm. GLC analyses were performed on a Varian 3700 flame ionization instrument (20 in. × 0.125 in. OV-101 5% on Chromosorb HP 100–120 mesh and 5 ft × 0.125 in. Carbowax 10% on DMCS 100–120 mesh columns) with Vista CDS 401 Varian chromatography data system. Decane, dodecane, and tetradecane were used as internal standard. Organic and inorganic reagents, ACS grade, were used without further purification. Aqueous sodium hypochlorite (15–18% active chlorine) was diluted at 0.35 M. The pH of the sodium hypochlorite was adjusted at 8.6 just before use by dissolving 50 mg/mL of solid $NaHCO_3$. 4-Methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl and 4-methoxy-1-oxo-2,2,6,6-tetramethylpiperidinium bromide were prepared following the procedure of Endo et al.[3c]

Oxidation of Alcohols to Carbonyl Derivatives: General Procedure. A 10-mL reaction flask thermostated at 0 °C was charged with 1.0 mL of a CH_2Cl_2 solution 0.8 M in the alcohol and 0.24 M in the appropriate internal standard, 1.0 mL of a 0.008 M CH_2Cl_2 solution of **3b** and 0.16 mL of a 0.5 M aqueous solution of KBr. At zero time 2.86 mL of 0.35 M aqueous sodium hypochlorite at pH 8.6 were added and the mixture stirred at 1300 rpm. Reactions were followed by GLC analysis. Results are reported in Table I. Oxidation of *p*-methoxybenzyl alcohol (entry 10) was achieved by using 0.5 mL of a 0.016 M CH_2Cl_2 solution of **3b** and 0.5 mL of a 0.08 M CH_2Cl_2 solution of Aliquat 336. Preparative runs were carried out on a fivefold scale; at the end of the reaction, the organic phase was separated, dried over $MgSO_4$, evaporated, and purified by column chromatography on silica gel.

Competitive Oxidation of 1-Nonanol and 2-Nonanol. A 10-mL reaction flask thermostated at 0 °C was charged with 1.0 mL of a CH_2Cl_2 solution containing 0.8 mmol of 1-nonanol, 0.8 mmol of 2-nonanol, 0.24 mmol of decane, 1.0 mL of a 0.008 M CH_2Cl_2 solution of **3b**, and 0.16 mL of a 0.5 M aqueous solution of KBr. A sample of 2.51 mL of 0.35 M aqueous sodium hypochlorite at pH 8.6 was added and the mixture stirred at 1300 rpm. After 3 min the hypochlorite was consumed, and the organic phase, analyzed by GLC, showed that 1-nonanol and 2-nonanol were 90% and 10% converted into the corresponding carbonyl derivatives, respectively.

Evaluation of the Amount of Oxidant in the Organic Phase. A 30-mL reaction flask thermostated at 0 or 25 °C was charged with 10 mL of a 0.008 M CH_2Cl_2 solution of **3b** and 0.40 mL of a 0.5 M aqueous solution of KBr. At zero time 14.3 mL of 0.35 M aqueous sodium hypochlorite at pH 8.6 was added and the mixture stirred at 1300 rpm. At the correct time, stirring was stopped. Aliquots (3 mL) of the organic solution were withdrawn and stirred with 20 mL of aqueous 10% KI and 1 mL of concentrated aqueous HCl for 10 min and then titrated with 0.01 N $Na_2S_2O_3$ aqueous solution with 1% aqueous solution of starch as indicator. Results are reported in Table III.

Oxidation of Alcohols and Aldehydes to Carboxylic Acids: General Procedure. A 10-mL reaction flask thermostated at 0 °C was charged with 1.0 mL of a 0.8 M CH_2Cl_2 solution in the alcohol (aldehyde) and 0.24 M in the appropriate internal standard, 0.50 mL of a 0.016 M CH_2Cl_2 solution of **3b**, 0.50 mL of a 0.08 M CH_2Cl_2 solution of Aliquat 336, and 0.16 mL of a 0.5 M aqueous solution of KBr. At zero time 5.72 mL (2.86 mL when the aldehyde was the substrate) of 0.35 M aqueous sodium hypochlorite at pH 8.6 was added and the mixture stirred at 1300 rpm. Samples of the reaction mixture withdrawn at different times were acidified and the organic phase analyzed by GLC. Results are reported in Table IV. Preparative runs were carried out on a fivefold scale; at the end of the reaction pH was adjusted at ≥12 with aqueous 2 N NaOH. The aqueous phase was separated, acidified with 6 N HCl, and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and evaporated. The residue was purified by crystallization or column chromatography on silica gel.

Acknowledgment. C.B. was the recipient of a grant sponsored by Montedipe S.p.A. (Milan). Special thanks are due to Dr. P. Roffia for helpful discussions.

(17) Semmelhack, M. F.; Schmid, C. R.; Cortês, D. A. *Tetrahedron Lett.* **1986**, *27*, 1119.

(18) These electronic effects contrast with the small influence of substituents observed in acetonitrile solution in the electrochemical catalytic cycle.[4,17]

(19) Under phase-transfer conditions the scarcely solvated anions[20] ClO^- and BrO^- must behave as strong bases, pK_a's of their conjugated acids being 7.53 and 8.69, respectively.[21]

(20) (a) Montanari, F.; Landini, D.; Rolla, F. *Top. Curr. Chem.* **1982**, *101*, 147 and references therein. (b) Dehmlow, E. V.; Dehmlow, S. S. *Phase-Transfer Catalysis*, 2nd ed.; Verlag Chemie: Weinheim, 1983.

(21) Weast, R. C. "*Handbook of Chemistry and Physics*", 55th ed.; CRC: Cleveland, 1974.

(22) A kinetic research is under study.