A New Oxidizing System for Aromatic Alcohols by the Combination of *N*-Oxoammonium Salt and Electrosynthesized Tetraalkylammonium Tribromide

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A combination of 2,2,6,6-tetramethyl-1-piperidinyloxyl and tetraalkylammonium tribromides (R_4NBr_3), which are available from the corresponding tetraalkylammonium bromides via electrooxidation with potassium bromide, has proved to be useful for oxidations of primary and secondary alcohols to the corresponding aldehydes and ketones, respectively. The oxidation reaction proceeds smoothly even with a 0.5—1.0 mol% of *N*-oxyl compounds and 1.5—2.0 equivalents of tetraalkylammonium tribromides in an aqueous-organic two-phase solution buffered at pH 8.0—8.6. This recyclable oxidant/co-oxidant combination system may involve the formation of *N*-oxoammonium salts, actual oxidizing agents of alcohols, by the action of hypobromite species generated from R_4NBr_3 in the binary solution. Utility of the method is highlighted by the selective oxidation of benzylic alcohols bearing electron-releasing groups on the aromatic nucleus to the corresponding aldehydes or ketones without any bromination and overoxidation.

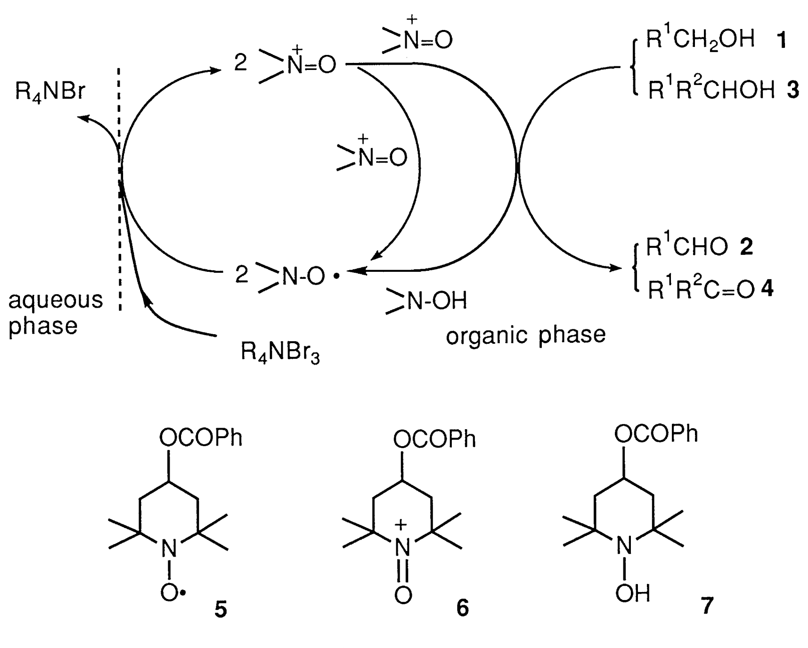
N-Oxoammonium salts have attracted increasing attention as a nonmetallic oxidizing reagent for alcohols to the corresponding carbonyl compounds.[1)] The attractiveness of this oxidant may stem from the following characteristic features: (a) the advantage of recycling the reagent by the aid of a co-oxidant (stoichiometric), (b) high selectivity attainable in favor of a primary hydroxyl group for the competitive oxidation of mixed polyols, and (c) easy operation and workup not to produce any hazardous wastes. In the preceding paper, we reported a catalytic procedure for the oxidation of alcohols by using the combination of *N*-oxyl compounds and co-oxidant such as sodium bromite ($NaBrO_2$) and calcium hypochlorite ($Ca(OCl)_2$).[1a)] However, this method was faced with a problem that undesired $NaBrO_2$-based bromination of the benzene nucleus proceeded considerably in competition with normal oxidation with *in situ* generated *N*-oxoammonium salts when aromatic alcohols bearing electron-releasing groups were oxidized. We, therefore, turned our attention to a new oxidizing system and examined the combination of *N*-oxyl compound and tetraalkylammonium tribromides (R_4NBr_3) as a co-oxidant for oxidation of aromatic alcohols, because these are considered to be more controllable than $NaBrO_2$ in terms of their reactivity.

Tetraalkylammonium tribromides (R_4NBr_3) have mainly been used for brominations of unsaturated compounds[2,3a)] and ketones,[3b)] and sometimes for the oxidation of amines[4)] and amides,[3c)] but, to the best of our knowledges, there was no precedent entry for a catalytic oxidation system. These tribromide salts are soluble in polar solvents such as CH_2Cl_2, $CHCl_3$, and AcOEt, but insoluble in H_2O, and exhibit long-term stability on exposure to air. Although tetraalkylammonium tribromides are available from the corresponding tetraalkylammonium bromides (R_4NBr) by various bromination methods,[2)] we employed an electrooxidation method for their preparation starting from tetraalkylammonium bromides and potassium bromide.[5)] R_4NBr_3 can undergo disproportionation in an aqueous basic solution to give hypobromite and Br^-, and hypobromite species thus generated is known to be a powerful oxidizing agent with redox potential of 0.71 V vs. NHE.[6)] Consequently, these properties of R_4NBr_3 are expected to be of benefit to the present purpose as a co-oxidant for *N*-oxoammonium-mediated oxidations, which indeed resulted in a dramatic improvement in circumventing the problem mentioned above.

Results and Discussion

In order to know a general trend for *N*-oxyl compound **5** (oxidant)/Bu_4NBr_3 (co-oxidant) combination, we firstly examined the oxidation of 1-undecanol (R^1=*n*-$C_{10}H_{21}$, **1a**) in an aqueous-organic two phase solution. To our delight, it turned out that the oxidation proceeded rather rapidly without any dimeric ester as a by-product (Scheme 1).

The reaction was carried out by employing 1.5—2.0 equivalents of Bu_4NBr_3 and a mixture of **1a** and **5** in a two phase solution consisted of CH_2Cl_2 and an aqueous buffer solution at 20 °C. Time-dependent curves of yields of the desired aldehyde **2a** (R^1=*n*-$C_{10}H_{21}$) are shown for various pH values in Fig. 1. The enhanced oxidizing ability of the combination of *N*-oxyl **5** and Bu_4NBr_3 is clearly indicated at pH 8.6 (aqueous $NaHCO_3$ solution) and more significantly at pH 8.0 (aqueous AcONa solution). An aqueous-organic two-phase solution was essential for the present purpose, otherwise no reaction was effected. Indeed, an attempted oxidation of **1a** in a single phase system of CH_2Cl_2 resulted in an almost quantitative recovery of **1a**. Neither higher (11) nor lower (4—7) pH than the values indicated above afforded the



Scheme 1.

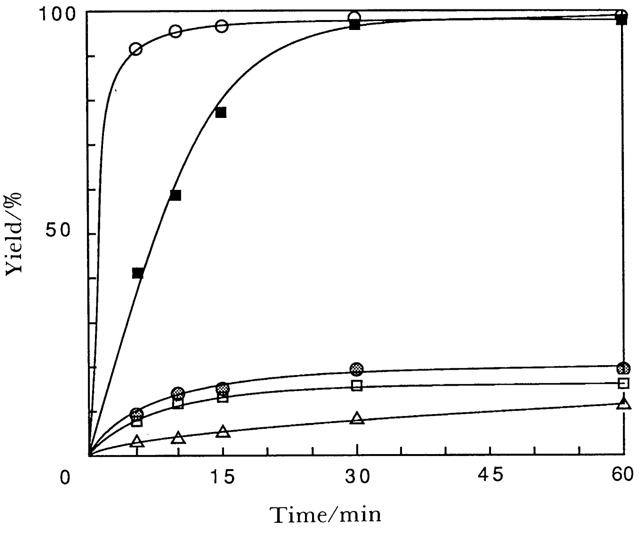


Fig. 1. Time-yield curves for the oxidation of **1a** with a **5**-Bu_4NBr_3 system under various pH values. Symbols are as follows: pH; 4 (△), pH; 7 (□), pH; 8.0 (○), pH; 8.8 (■), pH; 11 (●). Data points were obtained by GC analyses based on an internal standard (octyl acetate) method.

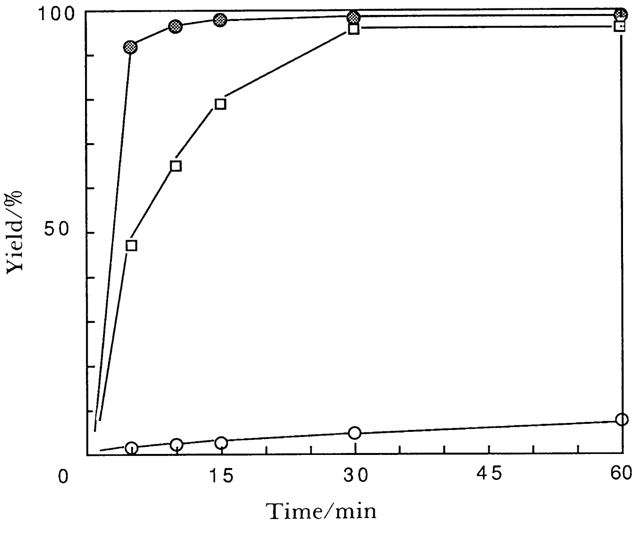


Fig. 2. Time-yield curves for the oxidation of **1a** and Bu_4NBr_3 (2.0 equiv) under various amounts of **5**. Symbols are as follows: 1 mol% of **5** (●); 0.5 mol% of **5** (□); in the absence of **5** (○). Analyzed by GC based on an internal standard (octyl acetate) method.

reasonable levels of yield, only reaching 20% or less. Furthermore, only 0.5—1.0 mol% of the *N*-oxyl compound **5** was enough for the oxidation to be completed within 35 minutes under the conditions indicated (Fig. 2).

Although the detailed mechanism on the present oxidation must wait future studies, we can point out its some aspects. Based on the amount of Bu_4NBr_3 as well as the fact that the oxidation can be enhanced in a two-phase solution buffered at pH 8.0—8.6, it is proposed that this reaction would involve the formation of hypobromite species from Bu_4NBr_3 at the initial stage.[7)] Thus, the disproportionation of Bu_4NBr_3 led to hypobromite HOBr as a source of positively charged bromine species, the reaction of which with **5** gave rise to *N*-oxoammonium salt that is responsible for the oxidation of substrates in the organic phase. In contrast to the trimeric structure of $NaBrO_2$[8)] as a versatile co-oxidant in the *N*-oxoammonium/*N*-oxyl redox system,[1a)] Bu_4NBr_3 dissolved in the organic phase of a binary system may exist as a monomer and be more stable than $NaBrO_2$.[7b)] In these respects R_4NBr_3 is highly amenable to the

Table 1. Oxidation of Aromatic Alcohols with **5** and Various Oxidizing Reagents[a)]

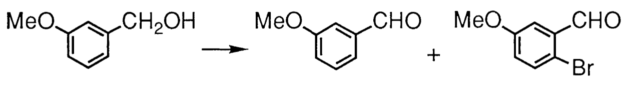
Entry	Substrate	Oxidizing reagents	Products (Yield/%)
1	**1b**	Bu_4NBr_3 (1.5 equiv)[b)]	**2b** (88) **8b** (—)
2	**1b**	$PhCH_2Bu_3NBr_3$ (1.5 equiv)[b)]	**2b** (87) **8b** (—)
3	**1b**	$NaBrO_2$ (5.0 equiv)[c)]	**2b** (39) **8b** (44)
4	**1b**	Electrolysis (4.0 F mol^{-1})[d)]	**2b** (9) **8b** (78)
5	**3a**	Bu_4NBr_3 (3.0 equiv)[b)]	**4a** (92) **9a** (—)
6	**3a**	Electrolysis (10.0 F mol^{-1})[d)]	**4a** (—) **9a** (87)

a) Substrates (1 mmol) were allowed to react in the presence of *N*-oxyl **5** (0.01 mmol). b) Carried out in a CH_2Cl_2–5% AcONa (6:14 v/v) solution. c) Carried out in a CH_2Cl_2–5% $NaHCO_3$ (5:10 v/v) solution. d) Electrolyzed in a CH_2Cl_2–25% NaBr (5:10 v/v)–(Pt) system.

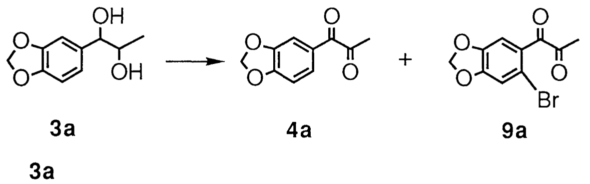
present redox system, which, in turn, implies that it can provide the splended oxidative ability.

In contrary to the selective oxidation with Bu_4NBr_3, our attempt to employ pyridinium tribromide ($Py\cdot HBr\cdot Br_2$) as an alternative co-oxidant for the present reaction system was unsuccessful. For instance, the similar oxidation of **1a** with a combination of **5** (catalytic) and $Py\cdot HBr\cdot Br_2$ (1.6 equivalent) was carried out in an aqueous 5% AcONa–CH_2Cl_2 system, affording a mixture of **2a** and the dimeric ester such as undecyl undecanoate, in 11% and 22% yields, respectively.

Since R_4NBr_3 is a good brominating agent applicable to a variety of unsaturated compounds including arenes,[2)] there is a fear of an unfavorable bromination on the aromatic ring in the oxidation of benzylic alcohols. However, the present oxidizing system consisted of an *N*-oxyl **5** (catalytic) and R_4NBr_3 (stoichiometric) turned out to be promising for the selective oxidation of various benzylic alcohols even though the aromatic rings were substituted with electron-releasing groups. In a previous work, we observed that bromination on the aromatic nucleus of *m*-methoxybenzyl alcohol (**1b**) became a predominant process (44% bromination in addition to 39% of the normal oxidation)[1a)] under the conditions employing *N*-oxyl **5** and $NaBrO_2$. It was also the case for an indirect electrooxidation with a two redox couples of *N*-oxoammonium/*N*-oxyl and [Br^+ or $Br^\bullet$]/Br^- (78% bromination).[9)] As shown in Entries 1 and 2, Table 1, to our delight, such a bromination process was almost completely suppressed by use of a combination of *N*-oxyl **5** and tetraalkylammonium tribromide such as Bu_4NBr_3 (88% yield) or $PhCH_2Bu_3NBr_3$ (87% yield).



1b **2b** **8b**

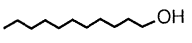
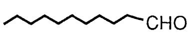
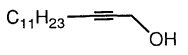
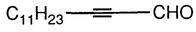
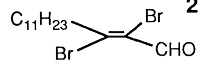
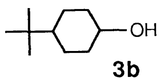
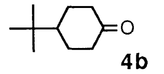
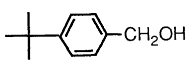
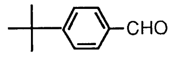
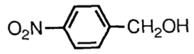
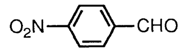
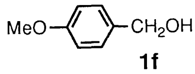
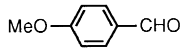
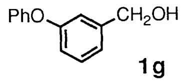
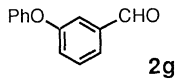
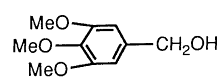
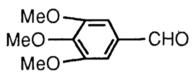
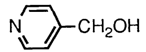
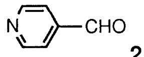
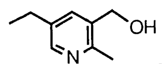
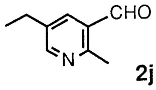


3a **4a** **9a**

3a

Furthermore, the oxidation of the aromatic diol **3a** by the combination of *N*-oxyl **5** and Bu_4NBr_3 afforded the corresponding 1,2-diketone **4a**, selectively (Entry 5),

Table 2. Oxidation of Primary and Secondary Alcohols by an *N*-Oxyl **5**-Bu_4NBr_3 System[a)]

Entry	Substrate	Bu_4NBr_3, equiv/reaction time/h	Product (Yield/%)[b)]
1	 **1a**	1.5/1.0	 **2a** (95)
2	 **1c**	2.3/1.0	 (16) **2c**  (79)
3[c)]	 **3b**	2.0/2.5	 **4b** (95)
4	 **1d**	1.5/1.0	 **2d** (93)
5	 **1e**	1.5/1.0	 **2e** (96)
6	 **1f**	1.5/1.0	 **2f** (92)
7	 **1g**	1.5/1.0	 **2g** (92)
8	 **1h**	1.5/2.0	 **2h** (76)[d)]
9	 **1i**	1.5/1.5	 **2i** (94)
10	 **1j**	1.5/1.5	 **2j** (90)

a) Substrates (1—2 mmol) were allowed to react with **5** (0.01—0.02 mmol) in a CH_2Cl_2 (3 ml)-aqueous 5% NaOAc system (7—14 ml). b) Yields based on isolated products. c) Aqueous saturated $NaHCO_3$ was used instead of aqueous 5% NaOAc. d) Contaminated with brominated product (18%).

while the indirect electrooxidation of **3a** with *N*-oxyl **5** as a mediator in an aqueous NaBr–CH_2Cl_2 solution resulted in the bromination concurrent with the oxidation to give **9a**, exclusively (Entry 6).

We applied this oxidation method to a variety of primary and secondary alcohols and the results are shown in Table 2. A triple bond adjacent to the hydroxyl group undergoes a competitive bromination under these conditions in the extent that products are consisted of an unseparable 17:83 mixture of the alkynal **2c** and 2,3-dibromo-2-tetradecenal (Entry 2). However, benzylic alcohols are oxidized to the corresponding aldehydes without any bromination on the rings. The yields are reproducible and as high as 90%. Some of the entries in Table 2 should be useful as an intermediate of agrochemicals (Entries 6 and 9) and drugs (Entry 7).

In conclusion, the present catalytic oxidation method is useful since R_4NBr_3 can easily be obtained by the electrooxidation of the corresponding R_4NBr with potassium bromide. Furtheremore, tetraalkylammonium bromide salts were recovered after the oxidation reaction by a chromatographic separation and then R_4NBr_3 were regenerated by their electrooxidation. This combined system of *N*-oxyl compound **5** and tetraalkylammonium tribromides can highly promote oxidation of alcohols as compared with the combination of **5** and $NaBrO_2$, which is advantageous in terms of durability of the recyclable *N*-oxyl compounds.

Experimental

All reactions were carried out under an argon atmosphere. Boiling points indicated by an air-bath temperature and melting points were uncorrected. Starting alcohols were purified by distillation or column chromatography (SiO_2) prior to use. GC analyses were carried out on a "Quadrex" Bond-Fused Silica capillary column (Methyl Silicone: 0.25 μm film thickness, 25 m×0.25 mm I. D.). ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$. Elemental analyses were performed in our laboratory.

Preparation of Tetrabutylammonium Tribromide. A cylindrical two compartment electrolysis cell, in which anodic room (200 ml volume) and the cathodic room (80 ml) were separated by a porous glass filter (20 mm in diameter, Type 5G). A platinum foil (4 cm×3 cm) and a lead plate (4 cm×3 cm) were used for the anode and the cathode, respectively. In the anodic compartment were placed Bu_4NBr (9.76 g, 30 mmol) and water (100 ml), and in the cathodic chamber were placed potassium bromide (3.57 g, 30 mmol) and water (40 ml). The mixture was electrolyzed at a constant current density of 25 mA cm^{-2} on warming at 40—50 °C. Orange crystals have precipitated on the surface of the anode upon charging the electricities and the reaction was terminated when 4 F mol^{-1} of electricity had been passed. To the anodic compartment was added CH_2Cl_2 (30 ml) to dissolve the orange solids and the aqueous phase was extracted with CH_2Cl_2. The combined extracts were dried ($MgSO_4$) and concentrated to dryness. The product was purified by recrystallization from CH_2Cl_2–Et_2O (1:1 v/v, 7 ml) to give 11.6 g (80%) of Bu_4NBr_3 as orange solids; mp 72—74 °C (lit,[11] 73—76 °C); IR (KBr) 2928, 2860, 1464, 1377, 1029, 880, 801, 741 cm^{-1}; ^1H NMR (200 MHz) δ=1.04 (t, 12, CH_3), 1.52 (m, 8, N–C–C–CH_2), 1.71 (m, 8, N–C–CH_2), 3.25 (t, 8, N–CH_2); ^{13}C NMR (50 MHz) δ=13.7, 19.8, 24.1, 59.1. Found: C, 39.9; H, 7.7; N, 3.0%. Calcd for $C_{16}H_{36}Br_3N$: C, 39.9; H, 7.5; N, 2.9%.

Similarly, benzyltributylammonium tribromide ($PhCH_2Bu_3NBr_3$) was obtained in 60—70% yields from $PhCH_2Bu_3NBr$; mp 93—94 °C; IR (KBr) 3382, 1481, 1470, 1458, 1406, 891, 777, 725, 704 cm^{-1}; ^1H NMR (500 MHz) δ=1.03 (t, 9, CH_3), 1.46 (m, 6, N–C–C–CH_2), 1.84 (m, 6, N–C–CH_2), 3.22 (m, 6, N–CH_2), 4.62 (s, 2, CH_2Ph), 7.47—7.51 (m, 5, ArH); ^{13}C NMR (126 Hz) δ=13.7, 19.8, 24.4, 58.7, 63.1, 126.6, 129.7, 131.1, 132.4.

Oxidation of Primary Alcohols to Aldehydes. A Typical Procedure. In a round-bottomed flask were succesively placed 1-undecanol (**1a**, 172 mg, 1.0 mmol), 4-benzoyloxy-2,2,6,6-tetramethyl-1-piperidinyloxyl (**5**, 2.8 mg, 0.01 mmol), and CH_2Cl_2 (3 ml). The mixture was covered with aqueous 5% CH_3CO_2Na (7 ml) and the tack was purged with argon. After agitating vigorously, to this mixture was added portionwise Bu_4NBr_3 (709 mg, 2.0 mmol). The mixture was stirred for 1 h at room temperature and the reaction was quenched with ethanol (0.2 ml). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined extracts were dried (Na_2SO_4), and concentrated. Flash chromatography (SiO_2, hexane–AcOEt 10:1 v/v) of the crude product gave 163 mg (95%) of undecanal (**2a**) as an oil; bp 113 °C (9 Torr, 1 Torr=133.322 Pa); IR (film) 2718, 1729 (C=O), 1466 cm^{-1}; ^1H NMR (500 MHz) δ=0.88 (t, *J*=7.0 Hz, 3, CH_3), 1.26 (brs, 14, CH_2), 1.62 (m, 2, CH_2), 2.41 (dt, *J*=7.3, 2.0 Hz, 2, CH_2CO), 9.76 (t, *J*=2.0 Hz, 1, CHO); ^{13}C NMR (126 MHz) δ=14.1, 19.2, 22.1, 22.7, 29.29, 29.34, 29.4, 29.5, 31.9, 43.9, 203.0.

Oxidation of Secondary Alcohols to the Ketones. A Typical Procedure. A solution of 4-*t*-butylcyclohexanol (**3b**, 156 mg, 1 mmol) and **5** (2.8 mg, 0.01 mmol) in CH_2Cl_2 (6 ml) was covered with aqueous saturated $NaHCO_3$ (12 ml). To this biphase mixture was added portionwise Bu_4NBr_3 (709 mg, 2.0 mmol) under a vigorous stirring at 40 °C. The mixture was stirred for an additional 2.5 h. The mixture was worked up in the usual manner and the crude products were purified by column chromatography to give 146 mg (95%) of 4-*t*-butylcyclohexanone (**4b**) as solids; mp 48—49 °C (from hexane) (lit,[16] 47.5—48.5 °C).

Properties and spectral data of the compounds in Table 1 and Table 2 are as follows.

3-Methoxybenzaldehyde (**2b**): Bp 141—142 °C (50 Torr) (lit,[12] 126—127 °C (25 Torr)).

4-Bromo-3-methoxybenzaldehyde (**8b**): Mp 71—73 °C (from hexane) (lit,[13] 74 °C); IR (KBr) 1601 (C=O), 1572, 1475, 1286, 934, 822, 648, 598 cm^{-1}; ^1H NMR (500 MHz) δ=3.828, 3.834 (s, 3, MeO), 7.01 (m, 1. ArH), 7.40 (m, 1, ArH), 7.45 (m, 1, ArH), 10.29 (d, *J*=4 Hz, 1, CHO); ^{13}C NMR (126 MHz) δ=55.7, 112.6, 117.9, 123.1, 133.9, 134.5, 159.2, 191.7.

A mixture of 2-Tetradecynal (**2c**)[14] and 2,3-Dibromo-2-tetradecenal: IR (film) 2858, 1700 (C=O), 1673, 1578, 1466, 1379, 1139, 1096 cm^{-1}; ^1H NMR (200 MHz, peaks due to the major component) δ=0.87 (t, *J*=6.7 Hz, 3), 1.26 (brs, 14, CH_2), 1.69 (m, 2, CH_2), 2.96, 3.00 (d, *J*=8.0 Hz, 2, CH_2), 9.81

(s, 1, CHO); ^{13}C NMR (50 MHz, peaks due to the major component) δ=14.1, 22.7, 27.2, 28.7, 29.25, 29.29, 29.4, 29.6 (2C), 31.9, 43.2, 120.7, 144.7, 185.6.

4-*t*-Butylbenzaldehyde (**2d**): Bp 89—90 °C (33 Torr).[15]

4-Nitrobenzaldehyde (**2e**): Mp 103—104 °C (lit,[16] 104—105 °C).

4-Methoxybenzaldehyde (**2f**): Bp 103—104 °C (33 Torr) (lit,[17] 248 °C).

3-Phenoxybenzaldehyde (**2g**): Bp 180—184 °C (14 Torr) (lit,[18] 175—176 °C (11 Torr)); IR (film) 3066, 2818, 2734, 1694 (C=O), 1582, 1483, 1452, 1390, 1164, 1131, 944 cm^{-1}; ^{1}H NMR (500 MHz) δ=7.04 (d, J=7.4 Hz, 2), 7.17 (t, J=7.4 Hz, 1), 7.29 (dd, J=7.8, 2.2 Hz, 1), 7.38 (t, J=7.8 Hz, 2), 7.46 (m, 1), 7.50 (t, J=7.8 Hz, 1), 7.60 (d, J=7.4 Hz, 1), 9.96 (s, 1, CHO); ^{13}C NMR (126 MHz) δ=118.1, 119.5, 124.2, 124.6, 124.7, 130.0, 130.4, 138.0, 156.2, 158.4, 191.6.

3,4,5-Trimethoxybenzaldehyde (**2h**): Mp 72—74 °C (lit,[19] 73—74 °C).

3-Pyridinecarbaldehyde (**2i**): Bp 83—85 °C (33 Torr) (lit,[20] 102—103 °C (20 Torr)).

5-Ethyl-2-methyl-3-pyridinecarbaldehyde (**2j**): Bp 115—117 °C (15 Torr) (lit,[1a] 115—117 °C (15 Torr)).

1-(3,4-Methylenedioxyphenyl)-1,2-propanedione (**4a**): Bp 108—111 °C (1 Torr) (lit,[21] 115—117 °C (1—2 Torr)); IR (film) 2916, 1715 (C=O), 1661 (C=O), 1605, 1506, 1491, 1446, 1354, 1267, 1038, 932 cm^{-1}; ^{1}H NMR (500 MHz) δ=2.49 (s, 3, CH$_3$), 6.07 (s, 2, CH$_2$), 6.87 (d, J=8 Hz, 1, PhH), 7.47 (d, J=1.6 Hz, 1, PhH), 7.62 (dd, J=8, 1.5 Hz, 1, PhH); ^{13}C NMR (126 MHz) δ=26.5, 102.1, 108.3, 109.0, 126.3, 128.0, 148.4, 153.1, 189.7, 200.8.

Recovery Experiment of Tetrabutylammonium Tribromide after the Oxidation Reaction of Alcohol. A mixture of EtOH (96 mg, 2.8 mmol) and the *N*-oxyl **5** (5.8 mg, 0.02 mmol) was treated with Bu$_4$NBr$_3$ (1.02 g, 2.12 mmol) in a suspension of CH$_2$Cl$_2$ (9 ml) and aqueous 5% AcONa (27 ml) for 30 min at room temperature. An aqueous phase was extracted with CH$_2$Cl$_2$ and the combined organic layers were dried (Na$_2$SO$_4$), and concentrated under vacuum. The residual solids were passed through a short column (SiO$_2$, AcOEt/hexane and then MeOH as an eluent) to give 657 mg of Bu$_4$NBr; IR (KBr) 2922, 2962, 2876, 1475, 1168, 1110, 897, 884, 739 cm^{-1}; ^{1}H NMR (500 MHz) δ=0.90 (t, J=7.4 Hz, 12, CH$_3$), 1.36 (m, 8, N-C-C-CH$_2$), 1.59 (m, 8, N-C-CH$_2$), 3.28 (m, 8, N-CH$_2$); ^{13}C NMR (126 MHz) δ=13.4, 19.5, 23.9, 58.7. Found: C, 59.2; H, 12.0; N, 4.3%. Calcd for C$_{16}$H$_{36}$BrN: C, 59.6; H, 11.3; N, 4.3%. The solids were electrolyzed with KBr (250 mg, 2.1 mmol) in water (50 ml) in the anodic compartment of the divided cell. Passage of 4.0 F mol^{-1} of electricity at 25 mA cm^{-2} at room temperature gave 663 mg (67%) of Bu$_4$NBr$_3$ as orange solids.

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