

Figure 2. The change of ultraviolet absorption spectra of the vesicle system which contained $\text{Ru}(\text{bipy})_2$ (lhcbipy) $^{2+}$, EDTA, and methyl viologen upon irradiation.

(Diocetadecyl dimethyl ammonium bromide) containing $\text{Ru}(\text{bipy})_2$ (lhcbipy) $^{2+}$, EDTA, and methyl viologen (System C).⁹

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6. This compound had mp. 78 °C; UV (CHCl_3) λ_{max} 300 nm; ^1H NMR (300 MHz, CDCl_3) δ 0.89 (t, $J=7.0$ Hz, 6H, CH_3), 1.10-1.60 (m, 52H, $-(\text{CH}_2)_{13}-$), 1.80 (q, $J=7.0$ Hz, 4H, $\text{O}-\text{CH}_2-\text{CH}_2-$), 4.40 (t, $J=7.0$ Hz, 4H, OCH_2), 7.90 (d, $J=6.0$ Hz, 2H, pyridine 6-H, 6'-H), 8.90 (d, $J=6.0$ Hz, 2H, pyridines-5-H, 5'-H), and 9.00 (s, 2H, pyridine 3-H, 3'-H). Anal. Calcd for $\text{C}_{44}\text{H}_{72}\text{N}_2\text{O}_4$: C, 76.25; H, 10.47; N, 4.04. Found.: C, 77.00; H, 10.77; N, 3.83.
7. This compound had mp. 242-244 °C; UV (CHCl_3) λ_{max} 478 nm; ^1H NMR (300 MHz, CDCl_3) δ 0.85 (t, $J=7.0$ Hz, 6H, terminal methyl), 1.22 (m, 52H, methylene), 1.76 (q, $J=7.0$ Hz, 4H, homomethoxy), 4.37 (t, $J=6.0$ Hz, 4H, methoxy), 7.50 (m, 4H, 5,5'-protons on bipyridine rings), 7.75 (d, $J=4.8$ Hz, 2H, 6,6'-protons on bipyridine with two substituents), 7.84 (d, $J=4.8$ Hz, 2H, 5,5'-protons on bipyridine with two substituents), 8.01 (t, $J=8.0$ Hz, 4H, 4,4'-protons on

bipyridine rings), 8.06 (d, $J=5.8$ Hz, 4H, 6,6'-protons on bipyridine rings), 8.39 (d, $J=8.0$ Hz, 3,3'-protons on bipyridine rings), 8.87 (s, 2H, 3,3'-protons on bipyridine with two substituents). Anal. Calcd for $\text{C}_{64}\text{H}_{88}\text{N}_6\text{O}_{12}\text{Cl}_2\text{Ru}$: C, 58.88; H, 6.79; N, 6.43. Found.: C, 59.05; H, 7.09; N, 6.28.

8. System A

An aqueous solution (1.0×10^{-4} M, 4 mL) of $\text{Ru}(\text{bipy})_2$ (lhcbipy) $^{2+}$ **6** was placed in test tube and sonicated at 70 °C for 20 min to prepare a vesicle solution. The vesicle solution (4 mL) was placed into UV cuvette (1 cm path, 4 mL). To the above solution, 20 μL of MV^{2+} (1.0×10^{-2} M) and 10 μL of EDTA (5.0×10^{-2} M) were added and then deaerated with argon for 20 min.

System B

An aqueous solution of $\text{Ru}(\text{bipy})_3^{2+}$ (1.0×10^{-4} M, 4 mL) was placed into UV cuvette (1 cm path, 4 mL). To the above solution, 20 μL of MV^{2+} (1.0×10^{-2} M) and 10 μL of EDTA (5.0×10^{-2} M) were added and then deaerated with argon for 20 min.

System C

A mixture of $\text{Ru}(\text{bipy})_2$ (lhcbipy) $^{2+}$ (1.0×10^{-4} M, 4 mL) and DODAB (5×10^{-5} M) was sonicated at 70 °C for 20 min. To above solution, 20 μL of MV^{2+} (1.0×10^{-2} M) and 10 μL of EDTA (5.0×10^{-2} M) were added and then deaerated with argon for 20 min.

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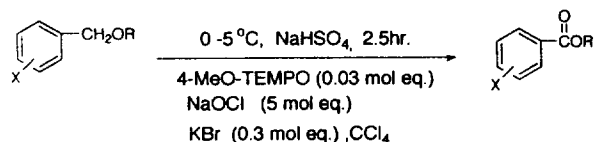
Oxidation of Benzyl Ethers with Sodium Hypochlorite Mediated by N-Oxoammonium Salt

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N-Oxoammonium salts (2,2,6,6-tetramethyl-1-oxopiperidinium salts) have been utilized as very reactive and selective oxidizing agents for alcohols,¹⁻⁶ diols,⁷ hydroxide ion,⁸ phosphines,⁹ phenols,⁹ amines,^{3,8-11} enolizable ketones,^{3,9} and indoles.¹² N-Oxoammonium salts have been used as oxidants in three different modes. First, they have been applied as pure compounds.¹⁻¹² Second, N-oxoammonium salts have been used as mediators. They have been reproduced from piperidine-1-oxyl radicals or their amines by a second oxidant *in situ*.¹³⁻¹⁹ The third mode is connected with the formation of oxoammonium salts from acid catalyzed disproportionation of piperidine-1-oxyl radicals.²⁰ However, it has been only known that N-oxoammonium salts oxidatively cleave benzyl ethers to benzaldehydes and the corresponding alkyl halides.²¹ Thus, we promptly decided to study on the oxidation of benzyl ethers with continuous generation of oxoammonium salt in the presence of catalytic amounts of 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-MeO-TEMPO,



Scheme 1. Reaction Conditions in Oxidation of Benzyl Ethers to Esters.

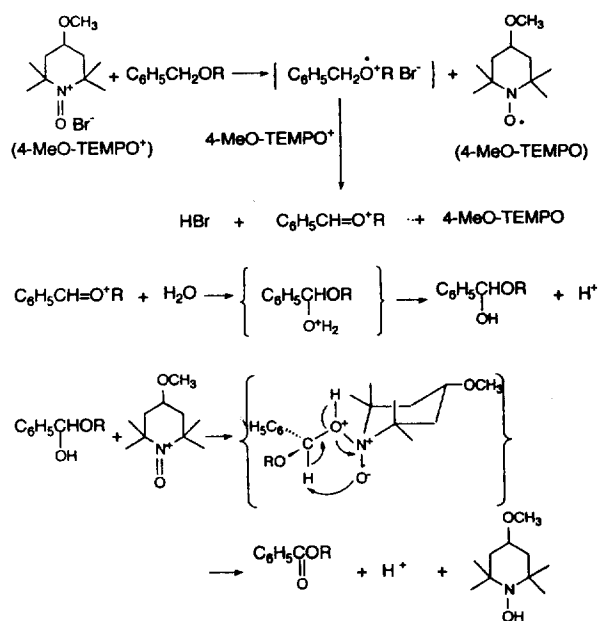
Table 1. Oxidation of Various Benzyl Ethers with Sodium Hypochlorite in the Presence of 4-MeO-TEMPO

Entry	XC ₆ H ₅ CH ₂ OCH ₂ R		Yield (%) ^a		
	X	R	Benzoate	Benzaldehyde	Benzoic acid
1	H	C ₆ H ₅	76	0	12
2	H	H	75	3	20
3	4-Cl	H	68	0	6
4	4-NO ₂	H	62	6	20
5	4-CH ₃	H	64	9	8

^aYields correspond to the isolated yield. The composition of products was calculated on the basis of either ¹H NMR or GC-mass data.

1) by sodium hypochlorite under aqueous organic two-phase reaction conditions. 4-MeO-TEMPO was prepared by Endo's method.⁹ All benzyl ethers were also synthesized in better than 90% yields from the corresponding benzyl alcohols with methyl iodide and sodium hydride in DME.^{22,23} The oxidation of benzyl ethers was carried out at 0-5 °C in CCl₄-aqueous NaOCl (5-6 mol equivalent) in the presence of 0.03 mol equivalent of the nitroxyl radical (1). The addition of 0.03 mol equivalent of KBr and adjustment of pH of the aqueous solution to less than pH 8.0 with NaHSO₄ were also required. Under these conditions, benzyl methyl ethers were mainly oxidized to methyl benzoates along with benzaldehydes and benzoic acids (see Scheme 1 and Table 1). Formates were not observed in the product mixtures. As shown in Table 1, the yields of oxidations to benzoates varied from 62 to 76% even though the reaction conditions were not optimized. The yields are isolated ones and the composition of the products was calculated on the basis of either ¹H NMR data or GC-mass data. Both methods gave an identical result. The ¹H NMR, IR spectra and GC data of products are in an excellent match with authentic samples and were used for the positive identification of the products. No oxidation to esters was observed in the absence of 4-MeO-TEMPO.

A typical oxidation procedure of benzyl ether is described as follows. Benzyl ether (4 mmol) and 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (22 mg, 0.12 mmol) were dissolved in carbon tetrachloride (13 mL) and combined with 1 mL of a 1.2 M aqueous solution of potassium bromide. NaHSO₄ (5 mmol) was added to adjust the pH value below 8.0 during the reaction. After cooling of the reaction mixture to 0-5 °C, aqueous sodium hypochlorite (0.86 M, 24 mL, 20.6 mmol) was added dropwise over a period of 2.5 hrs, and the reaction mixture was stirred for further 10 min. The organic phase was separated and the aqueous phase was



Scheme 2. Postulated Mechanism in Oxidation of Benzyl Ethers to Esters.

extracted with ethyl ether (10 mL) three times. The organic phase and the extracted ethyl ether were combined, the solution was washed with cold water, and dried over MgSO₄. After evaporating the solvent, the residue was analyzed by ¹H NMR or GC-mass and purified by either distillation or column chromatography (silica gel, eluent: hexane-ethyl acetate, 3:2). The aqueous layer was acidified with 6 N-HCl and extracted with ethyl ether to collect the acidic product. The physical and spectroscopic data of all isolated products are in agreement with those of authentic samples. The results are shown in Table 1.

N-Oxoammonium ion was suggested to be as an electron transfer agent in the mechanism of the oxidative cleavage of benzyl ethers to benzaldehydes and the corresponding alkyl halides.²¹ Initially, lone pair electron of ether may transfer to N-oxoammonium salt to produce a cation radical and second electron transfer may generate a cation. Deprotonation may subsequently be taken place to produce [PhCHO⁺-R] reaction intermediate. In the presence of water, this intermediate can be converted to a hemiacetal which is a postulated intermediate in electrochemical oxidation²² of benzyl ethers to esters. Thus, the oxidation of benzyl ethers to benzoates may be proceeded according to the reaction in Scheme 2.

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Table 1. Synthesis of 2,2-Disubstituted 3-Methyleneoxetanes **10**

Entry	Allylsilane 8	Yield (%) ^a	$\begin{matrix} \text{R}^1 \\ \text{R}^2 \end{matrix} \begin{matrix} \text{OH} \\ \text{Br} \end{matrix}$ (9)	$\begin{matrix} \text{R}^1 \\ \text{R}^2 \end{matrix} \begin{matrix} \text{Br} \\ \text{Br} \end{matrix}$ (11)	3-Methylene- oxetane 10	Yield (%)
			Yield(%) ^a	Yield(%) ^a		
a		63	98	—		91
b		33	88	—		73
c		54	85(38) ^b	—		76
d		38	88	—		73
e		48	59	32		77
f		78	73(49) ^b	21(49) ^b		92
g		61	74	20	—	—
h		62	71	27	—	—

**1****2****3****4****5**

Synthesis of 2,2-Disubstituted 3-Methyleneoxetanes

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Strained small oxacycles containing an exocyclic methylene group, methylene oxirane (allene oxide) **1**, α -methylene- β -lactone **2** and diketene **3** have been studied intensively by theoretical and synthetic chemists. Surprisingly, however, studies on methyleneoxetanes **4** and **5** have quite been ignored. Only the parent 3-methyleneoxetane **5** was synthesized from the retro Diels-Alder reaction of an anthracene ad-

duct⁵ and the interaction between the endocyclic oxygen and the methylene group of it was investigated by ultraviolet photoelectron spectra and molecular orbital calculations.⁶

In continuation of our studies on exploring synthetic application of 2-trialkylstannyl-3-trimethylsilylpropene **6**,⁷ we found a facile method for the synthesis of 2,2-disubstituted 3-methyleneoxetanes. Transmetalation of **6** with *n*-butyllithium provided 2-lithio-3-trimethylsilylpropene **7**, which reacted smoothly at -78°C with carbonyl compounds to produce 2-[(trimethylsilyl)methyl]allyl alcohols **8** in moderate yields. This route revealed much improved yield of **8a** compared to the reaction of the vinylolithium intermediate **7** generated from lithium halogen exchange of 2-bromoallylsilane by *t*-butyllithium with cyclohexanone⁸ (18%, cf. Table 1, entry a). When allyl alcohols **8a-d** were treated with a 10% excess