Hypervalent (*tert*-Butylperoxy)iodanes Generate Iodine-Centered Radicals at Room Temperature in Solution: Oxidation and Deprotection of Benzyl and Allyl Ethers, and Evidence for Generation of α-Oxy Carbon Radicals

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Abstract: 1-(*tert*-Butylperoxy)-1,2-benziodoxol-3(1*H*)-one (**1a**) oxidizes benzyl and allyl ethers to the esters at room temperature in benzene or cyclohexane in the presence of alkali metal carbonates. Since this reaction is compatible with other protecting groups such as MOM, THP, and TBDMS ethers, and acetoxy groups, and because esters are readily hydrolyzed under basic conditions, this new method provides a convenient and effective alternative to the usual reductive deprotection. Oxidation with **1a** occurs readily with C−H bonds activated by both enthalpic effects (benzylic, allylic, and propargylic C−H bonds) and/or polar effects (α-oxy C−H bonds), generating α-oxy carbon-centered radicals, which can be detected by nitroxyl radical trapping. Measurement of the relative rates of oxidation for a series of ring-substituted benzyl *n*-butyl ethers **2d** and **2p−s** indicated that electron-releasing groups such as *p*-MeO and *p*-Me groups increase the rate of oxidation, and Hammett correlation of the relative rate factors with the σ^+ constants of substituents afforded the reaction constant $\rho^+ = -0.30$. The large value of the isotope effect obtained for the oxidation of benzyl *n*-butyl ether **2d** ($k_H/k_D = 12-14$) indicates that the rate-determining step of the reactions probably involves a high degree of benzylic C−H bond breaking. The effects of molecular dioxygen were examined, and the mechanism involving the intermediacy of the *tert*-butylperoxy acetal **5** and/or the hydroperoxy acetal **32** is proposed. Particularly noteworthy is the finding that (*tert*-butylperoxy)iodane **1a** can generate the *tert*-butylperoxy radical and the iodine-centered radical **33a**, even at room temperature in solution, via homolytic bond cleavage of the hypervalent iodine(III)−peroxy bond.

Introduction

In spite of extensive studies on the chemistry of organoiodanes, little is known about peroxyiodanes, probably because of their high tendency to decompose.[1] Bis(peracyloxy)iodanes of the type $ArI(OOCOR)_2$ are believed to be an intermediate in the oxidation of iodoarenes to pentavalent arylperiodanes. In 1970, Plesnicar and Russell reported the first synthesis of (peraroyloxy)iodanes.[2] They obtained the symmetrically substituted [bis(perbenzoyloxy)iodo]benzenes as labile amorphous solids, which under spontaneous ignition or detonation upon manipulation in the solid state at room temperature, by the reaction of iodosylbenzene with perbenzoic acids. Derivatives of aliphatic peroxycarboxylic acids, being less stable, could not be isolated, and thus, reaction of iodosylbenzene with 40% peracetic acid at 35 °C gave pentavalent iodylbenzene via the transient formation of [bis(peracetoxy)iodo]benzene.[2b,3]

Milas and Plesnicar reported the reaction of iodosylbenzene with *tert*-butyl hydroperoxide in dichloromethane and proposed the in situ generation of labile [bis(*tert*-butylperoxy)iodo]benzene, which decomposes homolytically even at −80 °C to give *tert*-butylperoxy radical and iodobenzene.[4] This ready decomposition of the (alkylperoxy)iodane can be attributed to the small dissociation energy of the apical hypervalent peroxy−iodine(III) bond and is facilitated by conjugative overlap of the breaking hypervalent bond with π-orbitals of the aromatic nucleus. Recently, we reported the synthesis and characterization of the first stable crystalline (alkylperoxy)iodane, 1-(*tert*-butylperoxy)-1,2-benziodoxol-3(1*H*)-one (**1a**), in which fixation of an apical peroxy ligand and an equatorial aromatic ligand on iodine(III) by the formation of five-membered heterocycles such as an iodoxolone leads to enhanced stability of the (alkylperoxy)iodinanes:[5] Lewis acid-catalyzed ligand exchange of 1-hydroxy-1,2-benziodoxol-3(1*H*)-one with *tert*-butyl hydroperoxide in chloroform afforded the alkylperoxyiodane **1a** in

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(1) For reviews of organoiodanes, see: (a) Banks, D. F. *Chem. Rev.* **1966**, *66*, 243. (b) Koser, G. F. *The Chemistry of Functional Groups, Supplemented D*; Wiley: New York, 1983; Chapter 18. (c) Varvoglis, A. *Synthesis* **1984**, 709. (d) Ochiai, M.; Nagao, Y. *J. Synth. Org. Chem., Jpn.* **1986**, *44*, 660. (e) Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244. (f) Merkushev, E. B. *Russ. Chem. Rev.* **1987**, *56*, 826. (g) Ochiai, M. *Revs. Heteroatom Chem.* **1989**, *2*, 92. (h) Moriarty, R. M.; Vaid, R. K. *Synthesis* **1990**, 431. (i) Moriarty, R. M.; Vaid, R. K.; Koser, G. F. *Synlett.* **1990**, 365. (j) Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 274. (k) Varvoglis, A. *The Chemistry of Polycoordinated Iodine*; VHC Publishers: New York, 1992. (l) Koser, G. F. *The Chemistry of Functional Groups, Supplement D2*; Wiley: New York, 1995; Chapter 21.

(2) (a) Plesnicar, B.; Russell, G. A. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 797. (b) Plesnicar, B. *J. Org. Chem.* **1975**, *40*, 3267.

(3) Sharefkin, J. G.; Saltzman, H. *Org. Synth.* **1963**, *43*, 65.

(4) (a) Milas, N. A.; Plesnicar, B. *J. Am. Chem. Soc.* **1968**, *90*, 4450. (b) Traylor, T. G.; Xu, F. *J. Am. Chem. Soc.* **1987**, *109*, 6201. (c) Traylor, T. G.; Fann, W.-P.; Bandyopadhyay, D. *J. Am. Chem. Soc.* **1989**, *110*, 8009.

(5) Ochiai, M.; Ito, T.; Masaki, Y.; Shiro, M. *J. Am. Chem. Soc.* **1992**, *114*, 6269.

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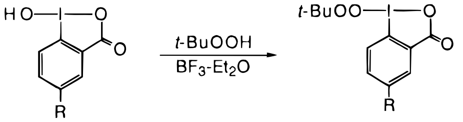
high yield. This is stable in the solid state and can be safely stored at room temperature for an indefinite period of time.[6]



1a: R = H
1b: R = NO_2

We report here that the (alkylperoxy)iodane **1a** oxidizes benzyl and allyl ethers to the esters even at room temperature in the presence of alkali metal carbonates, thus offering a new method for the deprotection of benzyl and allyl ethers. The oxidation of the activated C−H bonds with **1a** generates α-oxy carbon-centered radicals, which were detected by nitroxyl radical trapping. The large value of the isotope effect obtained for the oxidation of benzyl *n*-butyl ether **2d** indicates that the rate-determining step of the reactions probably involves a high degree of benzylic C−H bond breaking. We also examined the effects of molecular dioxygen on the reaction and propose a mechanism involving the intermediacy of *tert*-butylperoxy acetals and/or hydroperoxy acetals.

Results and Discussion

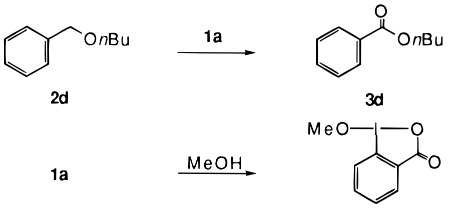
Optimization of Reaction Variables. The benzyl ether function is one of the most common protecting groups for alcohols, because of its ease of formation and stability to a variety of reagents and to both acidic and basic conditions. It is usually removed by catalytic hydrogenation or by alkali metal reduction.[7] If, however, the substrate contains additional reducible functions, this procedure may not be applied[8] and oxidative debenzylation is an alternative to the usual reductive methods.[9]

The oxidation of benzyl ethers to the corresponding esters of benzoic acids with the peroxyiodane **1a** takes place at room temperature; however, the reaction was found to be very slow. Oxidation of benzyl *n*-butyl ether **2d** was carried out in MeCN using 2.2 equiv of **1a** under nitrogen atmosphere using a rubber balloon. Even after 4 days at room temperature, 36% of **2d** was recovered unchanged and *n*-butyl benzoate **3d** was obtained in only 34% yield. As shown in Table 1, the benzylic oxidation is very sensitive to the nature of the solvents used. When the reaction was carried out in alcoholic solvents, such as methanol and *tert*-butyl alcohol, poor results were obtained. Extensive ligand exchange of the *tert*-butylperoxy group of **1a** with an alcohol would be responsible for low yields of the ester **3d**: in fact, treatment of **1a** with methanol at room temperature for 2 days gave the methoxyiodane **4**[10] in 50% yield. Use of diethyl ether as a solvent also gave poor results (Table 1, entry 7). Although all of the peroxyiodane **1a** was consumed after 24 h, **3d** was produced in less than 1% yield because of the oxidation of the solvent diethyl ether with **1a** under the conditions (for the oxidation of dialkyl ethers, see below).

Table 1. Solvent Effects in the Oxidation of Benzyl *n*-Butyl Ether **2d** with Peroxyiodane **1a**[a]

entry	solvent	ϵ	time (d)	yield of **3d** (%)[b]
1	MeCN	36.2	4	34 (36)
2	MeOH	32.6	4	12 (88)
3	*t*-BuOH	12.5	4.3	20 (67)
4	CH_2Cl_2	8.9	4	49 (4)
5	AcOEt	6.0	4	51 (14)
6	C_6H_5F[c]	5.42	4	47 (14)
7	Et_2O	4.2	1	<1 (95)
8	C_6H_6	2.27	4	70 (11)
9	C_6H_6[c]	2.27	4.3	83 (3)
10	C_6H_6[d]	2.27	3.2	11 (23)

[a] Unless otherwise noted, reactions were carried out using 2.2 equiv of **1a** at room temperature under nitrogen. [b] Yields were determined by GC. Parentheses are recovered **2d**. [c] 3 equiv of **1a** was used. [d] BF_3−Et_2O (0.1 equiv) was added.



2d **3d**
1a **4**

As shown in Table 1, oxidation of **2d** is very sensitive to solvent polarity. Solvents of low dielectric constants seem to give better results; in benzene (ϵ = 2.27), 70−83% yields of *n*-butyl benzoate **3d** were obtained (Table 1, entries 8 and 9). Addition of BF_3−Et_2O decreased the yield of **3d**. A good linear correlation between Dimroth's $E_T(30)$ values[11] (MeCN, 46.0; CH_2Cl_2, 41.1; AcOEt, 38.1; C_6H_6, 34.5) and the yields of **3d** [log (yields of **3d**)] was obtained ($n = 4$, $r = 0.98$). Oxidation of **2d** with **1a** in benzene resulted in a good yield of the ester **3d**; however, the rate of the reaction was too slow to be useful synthetically.

In the autoxidation of cumene, it has been shown that addition of bases such as Na_2CO_3, $NaHCO_3$, or $Ca(OH)_2$ increases both the rate of oxidation and the yields of the hydroperoxide product. These bases are thought to remove benzoic acid formed in the reaction as one of the byproducts.[12,13] In this peroxyiodane oxidation of benzyl ether **2d**, the formation of *o*-iodobenzoic acid, which is more acidic ($pK_a = 2.85$) than benzoic acid ($pK_a = 4.19$), from **1a** would also be expected. Furthermore, as was

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(6) Moss and Zhang also reported a synthesis of the peroxyiodane **1a** involving a ligand exchange of a labile (phosphoryloxy)iodane, prepared in situ by the reaction of 1-chloro-1,2-benziodoxol-3(1*H*)-one with silver diphenyl phosphate in DMSO, with *tert*-butyl hydroperoxide. See: Moss, R. A.; Zhang, H. *J. Am. Chem. Soc.* **1994**, *116*, 4471.

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(9) (a) RuO_4: Carlsen, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.* **1981**, *46*, 3936. Schuda, P.; F.; Cichowicz, M. B.; Heimann, M. R. *Tetrahedron Lett.* **1983**, *24*, 3829. (b) O_3: Hirama, M.; Shimizu, M. *Synth. Commun.* **1983**, *13*, 781. Angibeaud, P.; Defaye, J.; Gadelle, A.; Utille, J.-P. *Synthesis* **1985**, 1123. (c) CrO_3: Bal, B. S.; Kochhar, K. S.; Pinnick, H. W. *J. Org. Chem.* **1981**, *46*, 1492. (d) R_4N^+-MnO_4^-: Schmidt, H.-J.; Schafer, H. J. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 69. (e) DDQ: Oikawa, Y.; Yoshioka, T.; Yonemitsu, O. *Tetrahedron Lett.* **1982**, *23*, 885. (f) Me_2CO_2: Marples, B. A.; Muxworthy, J. P.; Baggaley, K. H. *Synlett* **1992**, 646. (g) Electrochemical: Weinreb, S. M.; Epling, G. A.; Comi, R.; Reitano, M. *J. Org. Chem.* **1975**, *40*, 1356.

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(12) Benzoic acid formed has been shown to decompose the hydroperoxide product. See: Tunoda, Y.; Matumoto, Y. *Kogyo Kagaku Zasshi* **1959**, *62*, 1555.

(13) On the other hand, photoinitiated benzylic bromination with bromotrichloromethane has been shown to be retarded by the addition of K_2CO_3, which could scavenge the hydrogen bromide produced in the reactions. For this bromination, both the trichloromethyl radical and the bromine atom, generated from hydrogen bromide, have been suggested to participate in benzylic hydrogen atom abstraction. See: (a) Tanner, D. D.; Arhart, R. J.; Blackburn, E. V.; Das, N. C.; Wada, N. *J. Am. Chem. Soc.* **1974**, *96*, 829. (b) Tanner, D. D.; Wada, N. *J. Am. Chem. Soc.* **1975**, *97*, 2190. (c) Krosley, K. W.; Gleicher, G. J. *J. Org. Chem.* **1990**, *55*, 4469.

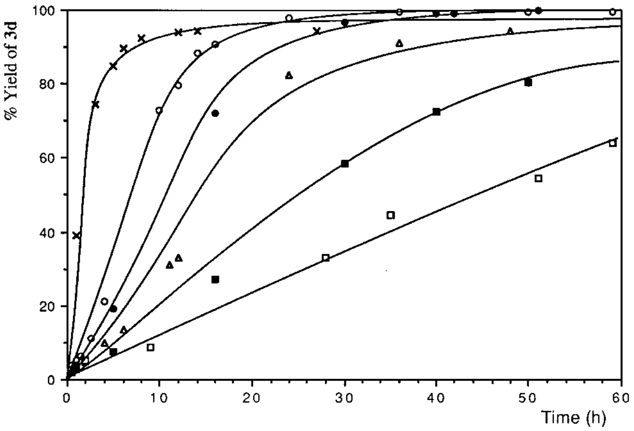


Figure 1. Time courses for oxidation of **2d** with **1a** (3 equiv) in the presence and absence of alkali metal carbonates (6 equiv) at 25 °C in benzene under nitrogen. Yields of **3d** were determined by GC. Symbols are as follows: (□) none, (■) Li_2CO_3, (△) Na_2CO_3, (●) K_2CO_3, (○) Rb_2CO_3, and (×) Cs_2CO_3.

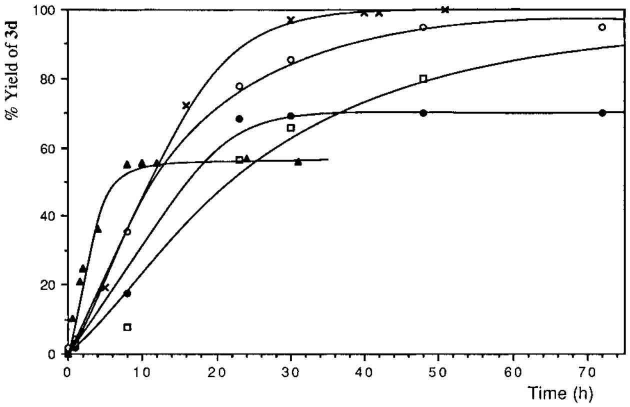


Figure 2. Time courses for the oxidation of **2d** with **1** in the presence of K_2CO_3 in benzene under nitrogen. Symbols are as follows: (●) **1a** (1 equiv)/K_2CO_3 (2 equiv)/25 °C, (○) **1a** (2 equiv)/K_2CO_3 (4 equiv)/25 °C, (×) **1a** (3 equiv)/K_2CO_3 (6 equiv)/25 °C, (▲) **1a** (2 equiv)/K_2CO_3 (4 equiv)/50 °C, (□) **1b** (2 equiv)/K_2CO_3 (4 equiv)/25 °C.

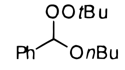
discussed above, addition of BF_3-Et_2O retards the oxidation. Accordingly, we examined the reaction in the presence of alkali metal carbonates as a base to remove acidic byproducts. Strong bases such as sodium and potassium hydroxides cause hydrolysis of the product esters and, therefore, are not suitable for this purpose.

We found that the use of alkali metal carbonates as an additive markedly accelerated the benzylic oxidation, although these bases are sparingly soluble in the solvent. The time courses of the reaction of **2d** with **1a** (3 equiv) in the presence and absence of various finely powdered alkali metal carbonates (6 equiv) in benzene at room temperature under nitrogen are shown in Figure 1. The rate of formation of the ester **3d** was increased considerably using Li_2CO_3 as an additive; for instance, yields of **3d** at the reaction time of 50 h increased from 55% (without Li_2CO_3) to 81% (with Li_2CO_3). Changing the metal cation of the carbonate additive from Li to Na, K, Rb, and Cs accelerated the rate of benzylic oxidation successively in the order of ascending atomic number. Use of Cs_2CO_3 proved to be most effective and afforded 93% yield of **3d** in less than 10 h at room temperature.

In contrast to the remarkable rate enhancement effected by K_2CO_3, no such result was observed when KCl, KBr, or KBF_4 was used as additives, clearly indicating that the counter cation itself shows negligible effects on the rate of this oxidation. Based on its powerful acceleration effect, its ease of handling, and its low cost, K_2CO_3 was used primarily in this study, although in some experiments Cs_2CO_3 was also used.

The stoichiometry of the reaction and the effects of the reaction temperature are shown in Figure 2. Oxidation with an equimolar amount of **1a** in the presence of K_2CO_3 afforded, after 24 h at 25 °C, a 69% yield of the ester **3d**. No improvement in product yield resulted from prolonged treatment (4 days at 25 °C), suggesting decomposition of **1a** to some extent under these conditions. Use of 2 equiv of **1a** after 2 days led to almost complete conversion of **2d** to give **3d** in 95% yield. Slightly higher yield of **3d** was obtained using 3 equiv of **1a**. When the reaction [**1a** (2 equiv)] was carried out at 50 °C and compared to the reaction at 25 °C, some rate acceleration was observed, especially at the beginning of the reaction; however, after 8 h [**3d** (55%) and **2d** (29%)], the reaction stopped and no further oxidation was observed. We interpret these results as indicating that the decomposition of **1a** in benzene at 50 °C is a relatively rapid process. Thus, **1a** (2 equiv)/K_2CO_3 (4 equiv)/25 °C/PhH/N_2 constituted our standard conditions. When the *p*-nitroperoxyiodane **1b**, prepared from 2-iodosyl-5-nitrobenzoic acid[14] by the ligand exchange reaction with *tert*-butyl hydroperoxide, was used instead of **1a**, the oxidation rate was slightly retarded (see Figure 2).

Substrate Generality. A. Oxidation of Benzyl Ethers. Because alkyl benzoates are readily hydrolyzed to the corresponding alcohols under basic conditions,[7] oxidation of benzyl ethers to the benzoate esters provides a method for the deprotection of benzyl ether protecting groups. To illustrate the utility of this reaction, we oxidized a wide range of benzyl ethers **2**. Table 2 shows the versatility of the peroxyiodane **1a** as an oxidizing reagent. Oxidation of benzyl ethers of methyl, primary, secondary, and tertiary alcohols **2a**−**n** occurred smoothly under our standard conditions, and good to excellent yields of the corresponding benzoate esters **3a**−**n** were obtained. In some cases, a small amount of deprotected alcohols and benzoic acid was obtained, due to partial hydrolysis of the esters during the reaction. In some reactions, formation of a small amount of *tert*-butylperoxy acetals was observed; for instance, in the reaction of **2d** (Table 2, entry 4) the peroxyacetal **5** was isolated in 3% yield in addition to **3d** (76%).



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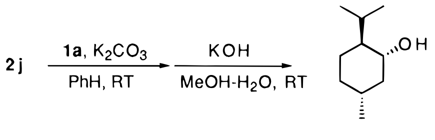
The isolation procedure of benzoate esters **3** is relatively simple. After filtration of an excess K_2CO_3 and potassium 2-iodobenzoate produced during the reaction from **1a**, silica gel chromatography gave pure esters **3**. Thus 1-menthyl benzoate **3j** was obtained from benzyl ether **2j** in 74% yield. Without isolation of the benzoate esters, hydrolysis of the crude reaction mixture gives the alcohols directly. After evaporation of the solvent, the reaction mixture of **2j** was treated with KOH in aqueous methanol at room temperature, leading directly to 1-menthol in 82% yield.



Oxidation of benzyl *n*-butyl ethers **2p**−**t** with electron-donating (MeO and Me) and electron-withdrawing groups (Cl and Ph) on the aromatic ring afforded high yields of the substituted benzoates **3p**−**t**. Oxidation of cyclic benzyl ethers

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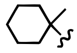
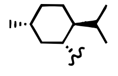
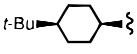
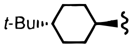
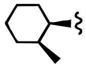
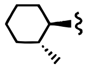
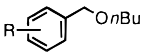
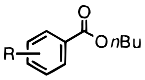
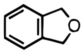
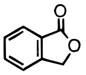
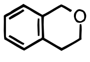
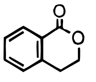
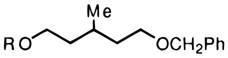
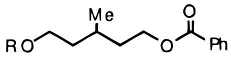
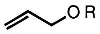
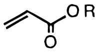
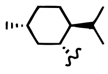
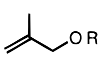
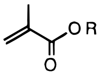
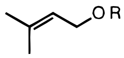
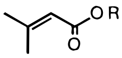
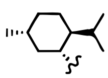
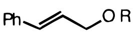
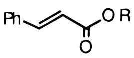
(14) (a) Willgerodt, C.; Gartner, R. *Chem. Ber.* **1908**, *41*, 2813. (b) Morrison, G. F.; Hooz, J. *J. Org. Chem.* **1970**, *35*, 1196.

Table 2. Benzylic Oxidation of Benzyl Ethers **2** with the Peroxyiodane **1a**[a]

entry	benzyl ether	2	time (h)	product	yield (%)[b]
	$PhCH_2OR$			$PhCO_2R$	
1	R= Me	**2a**	30	**3a**	(78)
2	Et	**2b**	36	**3b**	84
3	*iso*-Pr	**2c**	36	**3c**	71
4	*n*-Bu	**2d**	48	**3d**	76(95)
5	*sec*-Bu	**2e**	50	**3e**	63
6	*tert*-Bu	**2f**	24	**3f**	80
7	*cyclo*-C_5H_9	**2g**	34	**3g**	58
8	*cyclo*-C_6H_{11}	**2h**	48	**3h**	79
9		**2i**	31	**3i**	74
10		**2j**	30	**3j**	74
11		**2k**	36	**3k**	70
12		**2l**	33	**3l**	84
13		**2m**	36	**3m**	84
14		**2n**	30	**3n**	76
15	Ph	**2o**	103	**3o**	(21)[c]
					
16	R= *p*-MeO	**2p**	36	**3p**	(95)
17	*p*-Me	**2q**	31	**3q**	(82)
18	*p*-Cl	**2r**	51	**3r**	(94)
19	*m*-Cl	**2s**	56	**3s**	(98)
20	*p*-Ph	**2t**	48	**3t**	(94)
21		**2u**	23	 **3u**	78
22		**2v**	20	 **3v**	86
					
23	R= MOM	**2w**	72	**3w**	78
24	THP	**2x**	47	**3x**	61
25	TBDMS	**2y**	100	**3y**	68
26	Ac	**2z**	86	**3z**	90

[a] Unless otherwise noted, reactions were carried out using 2 equiv of **1a** and 4 equiv of K_2CO_3 in benzene at room temperature under nitrogen using a rubber balloon. [b] Isolated yields. Parentheses are GC yields. [c] **2o** (61%) was recovered.

Table 3. Allylic Oxidation of Allyl Ethers with Peroxyiodane **1a**[a]

entry	allyl ether		time (h)	product	yield (%)[b]
					
1	R= n-$C_{10}H_{21}$	**6a**	96[c,d]	**7a**	62
2	$Ph(CH_2)_2$	**6b**	42	**7b**	60
3	4-decyl	**6c**	80[d]	**7c**	45
4	3β-cholestanyl	**6d**	110	**7d**	62
5		**6e**	67	**7e**	42
6	1-adamantyl	**6f**	68	**7f**	50
7	4-*tert*-BuPh	**6g**	72	**7g**	10[e]
					
8	R= n-$C_{10}H_{21}$	**8**	72[d]	**9**	73
					
9	R= n-$C_{10}H_{21}$	**10a**	28[f]	**11a**	62
10	n-$C_{10}H_{21}$	**10a**	70[f,g]	**11a**	66
11	$Ph(CH_2)_2$	**10b**	46	**11b**	76
12		**10c**	67	**11c**	47
					
13	R= n-$C_{10}H_{21}$	**12**	51	**13**	72

[a] Unless otherwise noted, reactions were carried out using 2 equiv of **1a** and 2 equiv of Cs_2CO_3 at room temperature in cyclohexane under an atmosphere. [b] Isolated yields. [c] Reactions were carried out under nitrogen. [d] Instead of Cs_2CO_3, 4 equiv of K_2CO_3 was used. [e] **6g** (90%) was recovered. [f] 4 equiv of Cs_2CO_3 was used. [g] Instead of **1a**, 2 equiv of **1b** was used.

also took place; thus phthalan **2u** afforded phthalide **3u** (78%). Regioselective oxidation of isochroman **2v** at the benzylic methylene group attached to the ring oxygen was observed, and 1-isochromanone **3v** was obtained in an excellent yield. Benzyl aryl ethers were not readily oxidized under our standard conditions. The oxidation of phenyl ether **2o** is very slow and stops after stirring for 24 h (Table 2, entry 15), which makes possible selective oxidation of the alkyl ether **2h** in the presence of the phenyl ether **2o**. MOM, THP, and TBDMS ethers were found to be stable under standard conditions; thus the benzoates **3w**−**y** were obtained in good yields. The acetate protecting group (entry 26) was also unaffected. An efficient route is thus opened up for selective oxidation of the benzyl ether protecting group.

$$\mathbf{2h} + \mathbf{2o} \xrightarrow[\text{PhH, RT, 20 h}]{\mathbf{1a},\ K_2CO_3} \mathbf{2h} + \mathbf{3h} + \mathbf{2o} + \mathbf{3o}$$

Yield 27% 49% 84% 7%

B. Oxidation of Allyl Ethers. Allyl ethers are also used to protect alcohols, particularly in carbohydrate chemistry.[15] Deprotection of allyl ethers is usually achieved by heavy metal-catalyzed isomerization to the enol ethers with subsequent hydrolysis,[16] whereas the oxidative cleavage is very limited.[17] Allylic methylene groups of allyl ethers could be oxidized to a carbonyl group by the peroxyiodane **1a**. Using an alkali metal carbonate additive was again found to enhance the rate of oxidation, and both K_2CO_3 and Cs_2CO_3 were used in the allylic oxidation. As a solvent, cyclohexane afforded better yields of α,β-unsaturated esters than benzene. Thus, **1a** (2 equiv)/Cs_2CO_3 (2 equiv)/25 °C/cyclohexane/atmosphere was used as a standard procedure for oxidation of allyl alkyl ethers; the results are shown in Table 3.

Oxidation of allyl ethers **6** of primary, secondary, and tertiary alcohols under standard conditions afforded the α,β-unsaturated esters **7** in 40−60% yields. As observed in the case of benzyl phenyl ether **2o**, allylic oxidation of the allyl aryl ether **6g** is

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(15) (a) Gigg, R. *Am. Chem. Soc. Symp Ser.* **1977**, *39*, 253. (b) Gigg, R.; Conant, R. *Carbohydrate Res.* **1982**, *100*, C5.

(16) (a) Boss, R.; Scheffold, R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 558. (b) Corey, E. J.; Suggs, J. W. *J. Org. Chem.* **1973**, *38*, 3224. (c) Gigg, R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 738. (d) Ito, H.; Taguchi, T.; Hanzawa, Y. *J. Org. Chem.* **1993**, *58*, 774.

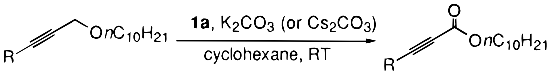
(17) Kariyone, K.; Yazawa, H. *Tetrahedron Lett.* **1970**, 2885.

Table 4. Oxidation of Hydrocarbons with the Peroxyiodane **1a**[a]

entry	hydrocarbon	time (h)	product	yield (%)[b]
1	indan	36	1-indanone	(75)
2	5-methoxyindan	18	5-methoxyindanone	50
			6-methoxyindanone	16
3	tetrahydronaphthalene	36[c]	α-tetralone	(66)
4	diphenylmethane	36	benzophenone	(98)
5	9,10-dihydroanthracene	24[d]	anthraquinone	89
6	anthrone	30	anthraquinone	84
7	xanthene	24	xanthone	92
8	fluorene (**18a**)	96[e]	9-fluoroenone (**19a**)	87
9	$Ph(CH_2)_5CH_3$ (**18b**)	82	$PhC(O)(CH_2)_4CH_3$ (**19b**)	(25)[f]

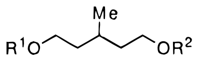
[a] Unless otherwise noted, reactions were carried out using 3 equiv of **1a** and 6 equiv of Cs_2CO_3 at room temperature in benzene under nitrogen. [b] Isolated yields. Parentheses are GC yields. [c] **1a** (2 equiv) and Rb_2CO_3 (4 equiv). [d] **1a** (4 equiv) and K_2CO_3 (8 equiv). [e] **1a** (2 equiv) and K_2CO_3 (4 equiv). [f] Hexylbenzene (**18b**, 75%) was recovered unchanged.

very slow and, even after prolonged treatment, only 10% of the ester **7g** was obtained. Oxidation of the methallyl **8**, prenyl **10**, and cinnamyl ethers **12** occurred smoothly and produced the conjugated esters **9**, **11**, and **13**, respectively, in moderate to good yields. Without isolation of the unsaturated esters, hydrolysis of the crude oxidation mixture directly gives the parent alcohols. For instance, when, after evaporation of the solvent, the reaction mixture of **6a** was treated with NaOH in aqueous methanol at room temperature, 1-decanol was isolated in 74% yield. Similarly, deprotection of allyl ethers **6e** and **10a** afforded menthol (68%) and 1-decanol (80%), respectively. Furthermore, propargylic oxidation of ether **14** with **1a** afforded the conjugated alkynyl ester **15** in moderate yields.



14a: R = H **15a** (51%)
14b: R = Et **15b** (61%)
14c: R = TMS **15c** (65%)

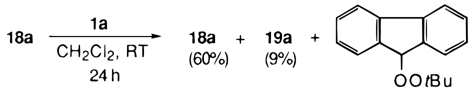
No chemoselectivity was observed in the attempted intramolecular competitions between benzylic and allylic oxidations of ethers. Thus ether **16a** with both allyloxy and benzyloxy groups in the molecule afforded a 1:1:2 mixture of the α,*β*-unsaturated ester **16b**, the benzoate **16c**, and the diester **16d** in 64% yield. Oxidation of **17a** with 4 equiv of **1a** gave the diester **17b** in 52% yield.



16a: $R^1 = H_2CCHCH_2$, $R^2 = PhCH_2$
16b: $R^1 = H_2CCHCO$, $R^2 = PhCH_2$
16c: $R^1 = H_2CCHCH_2$, $R^2 = PhCO$
16d: $R^1 = H_2CCHCO$, $R^2 = PhCO$
17a: $R^1 = Me_2CCHCH_2$, $R^2 = PhCH_2$
17b: $R^1 = Me_2CCHCO$, $R^2 = PhCO$

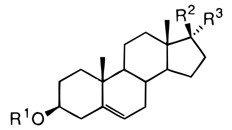
C. Oxidation of Arenes at the Benzylic Position. The peroxyiodane **1a** can be used to oxidize arenes at the benzylic position.[18] Oxidation of arenes was carried out in benzene in the presence of K_2CO_3 at room temperature. Indan was converted to 1-indanone, tetrahydronaphthalene to α-tetralone, diphenylmethane to benzophenone, 9,10-dihydroanthracene to anthraquinone, anthrone to anthraquinone, xanthene to xanthone, and fluorene (**18a**) to 9-fluorenone (**19a**). The yields are summarized in Table 4. The oxidation of 5-methoxyindan resulted in a higher yield of 5-methoxyindanone (50%) than 6-methoxyindanone (16%), thereby indicating that the methoxy group activates side chains in the *para* position to a greater extent than those in a *meta* position.

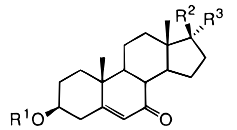
This oxidation of arenes yielding ketones was sometimes accompanied by the formation of some *tert*-butyl peroxides, particularly in the reaction with fluorene (**18a**). Exposure of **18a** to **1a** (1.3 equiv) in dichloromethane for 10 days gave 9-fluorenone (**19a**) in 84% yield; however, when the reaction was quenched after 1 day, 9-(*tert*-butylperoxy)fluorene **20** was obtained in 15% yield, along with 9-fluorenone (**19a**, 9%) and fluorene (**18a**, 60%). The peroxide **20**, on treatment with **1a** in dichloromethane, afforded 9-fluorenone (**19a**), indicating that the peroxide **20** would be a potential intermediate leading to the formation of **19a**. Similar observations on the formation of the peroxide **20** in chromium-catalyzed benzylic oxidation using *tert*-butyl hydroperoxide have been reported by Muzart.[19]



20 (15%)

The attempted allylic oxidation of simple alkenes gave poor results, and 1-eicosene [**1a** (2 equiv)/K_2CO_3 (4 equiv)/4 days] was recovered unchanged (95%). 3*β*-Acetoxy-5-androsten-17-one (**21a**), however, was readily oxidized at the C-7 allylic position and gave rise to the conjugated enone **22a**[19] in 81% yield. Cholesteryl acetate (**21b**) afforded the enone **22b** (62%). In the reaction of the benzyl ether **21c**, both the benzylic and allylic oxidations were observed and the keto ester **22c** was obtained in 55% yield.





21a: $R^1 = Ac$, $R^2, R^3 = O$
21b: $R^1 = Ac$, $R^2 = C_8H_{17}$, $R^3 = H$
21c: $R^1 = Bn$, $R^2 = C_8H_{17}$, $R^3 = H$

22a: $R^1 = Ac$, $R^2, R^3 = O$
22b: $R^1 = Ac$, $R^2 = C_8H_{17}$, $R^3 = H$
22c: $R^1 = COPh$, $R^2 = C_8H_{17}$, $R^3 = H$

Radical Trapping. Isolation of the peroxides **5** and **20** in the benzylic oxidations suggests the involvement of radical species. Addition of an equivalent amount of *p*-methoxyphenol (which has been shown to be a good radical inhibitor[20]) in the reaction of **2d** with **1a** completely inhibits the benzylic oxidation (Table 5, entry 5).[21] The use of a less than stoichiometric amount of *p*-methoxyphenol relative to **1a** partly inhibits the oxidation. A similar type of inhibition was observed using α-tocopherol as an additive.[22] Effective inhibition of the oxidation was also observed on addition of galvinoxyl, which is an efficient scavenger for both oxygen- and carbon-centered

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(18) (a) Zhao, D.; Lee, D. G. *Synthesis* **1994**, 915. (b) Pearson, A. J.; Han, G. R. *J. Org. Chem.* **1985**, *50*, 2791. (c) Murahashi, S.; Oda, Y.; Naota, T.; Kuwabara, T. *Tetrahedron Lett.* **1993**, *34*, 1299. (d) Barton, D. H. R.; Wang, T.-L. *Tetrahedron Lett.* **1994**, *35*, 5149.

(19) Muzart, J. *Tetrahedron Lett.* **1986**, *27*, 3139.

(20) Li, P.; Alper, H. *J. Mol. Catal.* **1992**, *72*, 143.

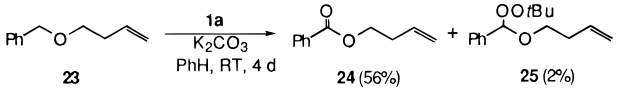
Table 5. Oxidation of Benzyl *n*-Butyl Ether **2d** with Peroxyiodane **1a**[a]

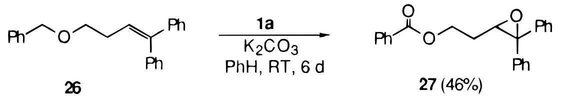
							product yield (%)[b,c]		
entry	**2d** (equiv)	**1a** (equiv)	K_2CO_3 (equiv)	additive (equiv)	conditions[d]	time (h)	**3d**	**5**	**2d**
1	1	1	2		30 °C, N_2[e]	48	70	3	14
2	1	1	2		30 °C, O_2	48	67	2	24
3	1	1	2		30 °C, Ar[e]	72	30	49	21
4	1	1	0		30 °C, Ar[e]	72	14	11	54
5	1	1	2	*p*-methoxyphenol (1)	30 °C, N_2	48	0	−	100
6	1	1	2	α-tocopherol (1)	30 °C, N_2	48	3	−	90
7	1	2	4		30 °C, N_2[e]	48	90	2	5
8	1	2	4		30 °C, O_2	48	90	1	5
9	1	2	4		30 °C, Ar[e]	72	62	28	2
10	1	2	0		30 °C, Ar[e]	72	23	32	25
11	1	2	4	*p*-methoxyphenol (1)	30 °C, N_2	48	46	−	38
12	1	2	4	α-tocopherol	30 °C, N_2	48	53	−	43
13	1	2	4	galvinoxyl (2)	30 °C, N_2	48	5	−	95
14	1	2	4	nitrobenzene (2)	30 °C, N_2	48	95	−	5
15	25	1	2		30 °C, N_2	410	596	−	−
16	25	1	2		30 °C, O_2	410	638	−	−
17	25	1	2		30 °C, Ar	450	24	72	−

[a] Reactions were carried out in benzene. [b] GC yields. Parentheses are NMR yields; "−" denotes that yields were not determined. [c] Yields of entries 1−14 and 15−17 are based on benzyl *n*-butyl ether **2d** and the peroxyiodane **1a**, respectively. [d] N_2: under dinitrogen rubber balloon. O2: under dioxygen rubber balloon. Ar: in a degassed argon sealed tube. [e] Iodane was recovered as 1-chloro-1,2-benziodoxol-3(1*H*)-one, and the yields based on **1a** are: 30% (entry 1), 4% (entry 3), 30% (entry 4), 25% (entry 7), 29% (entry 9), 40% (entry 10).

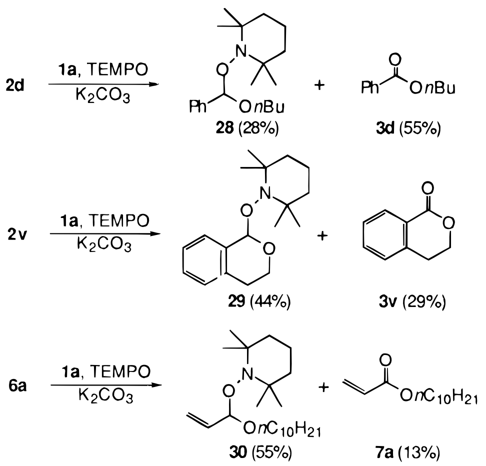
radicals (Table 5, entry 13).[23,24] On the other hand, no inhibition was observed in the presence of nitrobenzene, often used as a radical inhibitor.[25]

To establish the generation of radicals at benzylic positions, appropriate radical probe substrates **23** and **26**, which are based upon the familiar 5-*exo-trig* cyclizations of the parent and substituted 5-hexenyl radicals, were synthesized.[26,27] Reaction of **23** with **1a**, however, proceeded without detectable cyclization and afforded the ester **24** (56%) along with a small amount of the peroxyacetal **25** (2%).[28] Attempted cyclization of the more efficient radical probe **26**[29] gave the epoxy ester **27** without the formation of cyclization products. The selective formation of the epoxy ester **27** may be due to the more rapid oxidation of the trisubstituted double bond with two phenyl groups compared to the benzylic oxidation. Reductive removal of benzyl ether protecting groups by catalytic hydrogenation is not compatible with the presence of olefins. That the terminal monosubstituted double bond remains unchanged in the reaction of **23** is indicative of the possibility that chemoselective deprotection of a benzyl group may occur in the presence of isolated monosubstituted double bonds.





Rate constants for alkyl radical coupling with nitroxyl radicals are very large and relatively insensitive to the carbon radical stability. Therefore, the nitroxyl radical coupling method is most useful for studies of fast radical reactions.[27] The reaction of benzyl *n*-butyl ether **2d** with **1a** in the presence of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) under an argon atmosphere resulted in a competition between a TEMPO trap of the free radicals generated and the normal oxidation to the ester; thus the TEMPO adduct **28** was obtained in 28% yield along with the ester **3d** (55%). In the reaction of isochroman **2v**, the TEMPO adduct **29** was obtained as a major product in 44% yield. Furthermore, the TEMPO adduct **30** was obtained in good yield from the allylic oxidation of the ether **6a**. These results clearly indicate the intermediacy of benzylic and allylic radicals in the oxidation with **1a**.



The formation of both the TEMPO adducts and esters or lactones in these reactions implies that the rate constant for the reaction of benzyl radicals with **1a**, which leads to the formation of normal oxidation products (see below), would be of the same order of magnitude as the rate constant for the reaction of benzyl

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(21) It is not at all clear whether or not the added *p*-methoxyphenol traps radicals generated in the reaction. We found that oxidation of phenols with the peroxyiodane **1a** takes place, and the results will be reported elsewhere.

(22) For peroxy radical-trapping with α-tocopherol, see: (a) Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 6478. (b) Jackson, R. A.; Hosseini, K. M. *J. Chem. Soc.*, *Chem. Commun.* **1992**, 967.

(23) Bartlett, P. D.; Funahashi, T. *J. Am. Chem. Soc.* **1962**, *84*, 2596.

(24) Furthermore, added galvinoxyl completely inhibits the oxidation of the allyl ether **6a**.

(25) Stavber, S.; Planinsek, Z.; Zupan, M. *J. Org. Chem.* **1992**, *57*, 5334.

(26) Motherwell, W. B. Crich, D. *Free Radical Chain Reactions in Organic Synthesis*; Academic Press: New York, 1992.

(27) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151.

(28) For 5-*exo* cyclizations of 1-phenyl-5-hexenyl radicals, see: (a) Walling, C.; Cioffari, A. *J. Am. Chem. Soc.* **1972**, *94*, 6064. (b) Pines, H.; Sih, N. C.; Rosenfield, D. B. *J. Org. Chem.* **1966**, *31*, 2255.

(29) The first order cyclization rate constants at 25 °C for the 5-hexenyl and 6,6-diphenyl-5-hexenyl radicals are 2.3×10^5 s^{-1} and 5×10^7 s^{-1}, respectively. See: (a) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739. (b) Ha, C.; Horner, J. H.; Newcomb, M.; Varick, T. R.; Arnold, B. R.; Lusztyk, J. *J. Org. Chem.* **1993**, *58*, 1194. (c) Newcomb, M.; Horner, J. H.; Shahin, H. *Tetrahedron Lett.* **1993**, *34*, 5523.

Table 6. Relative Reactivity of Benzyl Ethers **2** and Related Compounds with **1a** at 30 °C

substrate	k_{rel}	substrate	k_{rel}
2p (*p*-MeO)	1.93 ± 0.16	**18b** $Ph(CH_2)_5CH_3$	0.12
2q (*p*-Me)	1.15 ± 0.05	(n-Bu)$_2$O	0.05
2d (H)	1.0		
2r (*p*-Cl)	0.96 ± 0.03		
2s (*m*-Cl)	0.84 ± 0.02		

radicals with TEMPO ($k \approx 10^8$ M^{-1} s^{-1}).[30] These results strongly suggest that the attempted 5-*exo*-cyclization of the benzyl radical derived from **23** could not have competed with the reaction with **1a** leading to the formation of the ester **24**, since the reaction was carried out at a concentration of 0.1 M for **1a**.[29] Furthermore, compared to 5-hexenyl radical, a substantially reduced rate constant for cyclization of 2-oxa-5-hexenyl radical ($k = 5 \times 10^4$ s^{-1} at 25 °C) has been reported,[31,32] which probably shows the cyclization of the benzyl radical derived from **26** also could not compete with the reaction with **1a**. This reduced rate constant has been attributed to an increased activation energy required to adopt a conformation for cyclization in which resonance between the radical center and the oxygen atom is lost.

Substituent Effect. To gain further insight into the mechanism of the oxidation of benzyl ethers by the peroxyiodane **1a**, the relative rates of oxidation for a series of ring-substituted benzyl butyl ethers **2d** and **2p**−**s** were measured under argon at 30 °C in benzene by competitive reactions, in which a mixture of each 25-fold excess of two competing substrates was used. Table 2 shows that benzoate esters **3d** and **3p**−**s** were formed in high yields, regardless of the substitution of the phenyl ring. Electron-releasing groups such as *p*-MeO and *p*-Me groups increase the rate of oxidation; the effect of substituents on the rate of oxidation is shown in Table 6. Hammett correlation plot for the oxidation of these benzyl butyl ethers presented in Table 6 showed a better correlation of relative rate factors with the σ^+ rather than the σ constants of substituents in the aromatic ring and afforded the reaction constant $\rho^+ = -0.30$ ($r = 0.97$).[33] This ρ^+ value appears to be comparable to $\rho^+ = -0.65$ for benzylic hydrogen abstractions from dibenzyl ethers by benzoyloxy radical.[34]

A reasonable rate of oxidation of methylene groups to carbonyl groups requires the presence of both the phenyl and alkoxy groups (see Table 6). When oxygen of **2d** was replaced by a methylene group, the rate of oxidation decreased to one-tenth. Similarly, dibutyl ether is 20 times less reactive than **2d**. These relative reactivities appear to correlate well with their respective C−H bond dissociation energies:[35] **H**−**C**H(OMe)-Ph (77 kcal mol^{-1}), **H**−**C**H(CH_3)Ph (85.4 kcal mol^{-1}), and **H**−**C**H(CH_3)OEt (91.7 kcal mol^{-1}).

Deuterium Isotope Effect. To obtain the deuterium isotope effect, the relative rate constant for the competitive oxidation of *m*-chloro ether **2s** vs n-$BuOCD_2Ph$ (**2d**-d_2) was measured ($k_{2s}/k_{2d\text{-}d_2} = 10.2$) under argon at 30 °C in benzene and compared with the relative rate $k_{2s}/k_{2d} = 0.84$ in Table 6. A very large deuterium kinetic isotope effect $k_H/k_D = 12$ was obtained. This large isotope effect was further confirmed by the competition of *p*-chloro ether **2r** vs **2d**-d_2, which resulted in the value $k_H/k_D = 14$. The average isotope effect of 13 is very large. Similarly, very large isotope effects have been reported for the radical abstraction of hydrogen from tetralin (k_H/k_D; 16) and cumene (k_H/k_D; 20) by *tert*-butylperoxy radicals,[36] for the generation of benzylic radical from 10-methyl-9,10-dihydroacridine (k_H/k_D; 21) by aminoxyl radicals,[37] and for formation of the allylic hydroperoxide from linoleic acid by soybean lipoxygenase.[38] This large value of isotope effect obtained for oxidation of benzyl butyl ether **2d** indicates that the rate-determining step of the reactions probably involves a high degree of benzylic C−H bond breaking.

Effects of Molecular Dioxygen and Characterization of Reaction Intermediates. Effects of molecular dioxygen in the reaction of **2d** with **1a** were examined, and the results are summarized in Table 5. No differences in the yields and product profiles were observed between the reactions carried out under dinitrogen rubber balloon and dioxygen rubber balloon. However, when the reaction was carried out in a degassed argon sealed tube, the yield of the ester **3d** decreased to a great extent, and a large amount of the peroxyacetal **5** was produced (Table 5, entries 1−3, and 7−9). Atmospheric dioxygen has been shown to penetrate into a rubber balloon,[39] which, in turn, leads to the same results in the product profiles and the yields of the reactions under dinitrogen rubber balloon and under dioxygen rubber balloon. Very interestingly, in the presence of a 25-fold excess of **2d** relative to **1a**, the prolonged reactions (410 h) under dinitrogen as well as dioxygen balloons afforded more than stoichiometric amounts of **3d** (*ca*. 600%), while the reaction in the absence of dioxygen (a degassed argon tube experiment) gave 24% of **3d** and 72% of **5** even after 450 h (Table 5, entries 15−17). These results clearly show that the presence of oxygen will be required for facile oxidation of **2d** to the ester **3d** by the peroxyiodane **1a**. As shown in Table 5, in the reaction under an argon atmosphere, adding K_2CO_3 enhanced the rate of benzylic oxidation.

It is significant that a large amount of the peroxyacetal **5**, whose structure was unambiguously established by the synthesis from di-*n*-butyl acetal **31** via ruthenium(III)-catalyzed acetal exchange reaction,[40] was isolated in the reactions under an argon atmosphere. As discussed above, the *tert*-butyl peroxide **20** appears to be an intermediate for the oxidation of fluorene (**18a**) to 9-fluorenone (**19a**) with **1a**. Furthermore, *tert*-butylperoxy acetals have been shown to undergo base-catalyzed decomposition to esters in high yields,[41] and, therefore, we regard it as important to investigate the possibility of decomposition of the peroxy acetal **5** to the ester **3d** under the conditions. As shown in Table 7, the peroxyacetal **5** was stable in benzene toward *o*-iodobenzoic acid, which is produced during the benzylic oxidation of **2d** with **1a**, whereas formation of the ester **3d**, albeit in low yields, resulted from the reaction with either K_2-

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[30] (a) Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4983. (b) Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4992.

[31] Beckwith, A. L. J.; Glover, S. A. *Aust. J. Chem.* **1987**, *40*, 157.

[32] On the other hand, the cyclization rate constants of 1-methoxy-5-hexenyl radicals have been shown to be nearly equal to those for related alkyl radicals lacking the methoxy group. See: (a) Johnson, C. C.; Horner, J. H.; Tronche, C.; Newcomb, M. *J. Am. Chem. Soc.* **1995**, *117*, 1684. (b) Newcomb, M.; Filipkowski, M. A.; Johnson, C. C. *Tetrahedron Lett.* **1995**, *36*, 3643.

[33] Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.

[34] (a) Huang, R. L.; Lee, H. H.; Ong, S. H. *J. Chem. Soc.* **1962**, 3336. (b) Russell, G. A.; Williamson, R. C. *J. Am. Chem. Soc.* **1964**, *86*, 2357.

[35] (a) Lide, D. R., Ed. CRC *Handbook of Chemistry and Physics*, 73rd ed.; CRC Press: Boca Raton, FL, 1992; pp 9−138. (b) Baciocchi, E. *Acta Chem. Scand.* **1990**, *44*, 645.

[36] (a) Howard, J. A.; Ingold, K. U.; Symonds, M. *Can. J. Chem.* **1968**, *46*, 1017. (b) Russell, G. A. *J. Am. Chem. Soc.* **1957**, *79*, 3871.

[37] Fukuzumi, S.; Tokuda, Y.; Chiba, Y.; Greci, L.; Carloni, P.; Damiani, E. *J. Chem. Soc., Chem. Commun.* **1993**, 1575.

[38] Glickman, M. H.; Wiseman, J. S.; Klinman, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 793.

[39] Sasai, H. *Farumashia* **1992**, *28*, 581.

[40] (a) Murahashi, S.; Oda, Y.; Naota, T. *Chem. Lett.* **1992**, 2237. (b) Rieche, A.; Schmitz, E.; Beyer, E. *Chem. Ber.* **1958**, *91*, 1942.

[41] (a) Mukaiyama, T.; Kato, J.; Miyoshi, N.; Iwasawa, N. *Chem. Lett.* **1985**, 1255. (b) Mukaiyama, T.; Miyoshi, N.; Kato, J.; Ohshima, M. *Chem. Lett.* **1986**, 1385. (c) Ganem, B.; Heggs, R. P.; Biloski, A. J.; Schwartz, D. R. *Tetrahedron Lett.* **1980**, *21*, 685.

Table 7. Reaction of *t*-Butylperoxy-**5** and Hydroperoxyacetals **32**

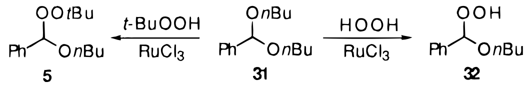
$$\mathbf{5}\ \text{or}\ \mathbf{32}\ \xrightarrow[\substack{\text{N}_2}]{}\ \mathbf{3d}$$

$$\underset{\text{PhH, 30 °C, 3 day}}{}$$

			product yield (%)[a]	
entry	acetal	additive (equiv)	**3d**	acetal
1	**5**	none	3	97
2	**5**	*o*-iodobenzoic acid (1)	1	80
3	**5**	K_2CO_3 (6)	7	93
4	**5**	**1a** (1)	21	74
5	**5**	**1a** (1), K_2CO_3 (2)	20	80
6	**32**	none	0	100
7	**32**	*o*-iodobenzoic acid (1)	1	79
8	**32**	K_2CO_3 (6)	44	27
9	**32**	**1a** (1)	66	5

[a] Yields of entries 1−5 and 6−9 were determined by GC and NMR, respectively.

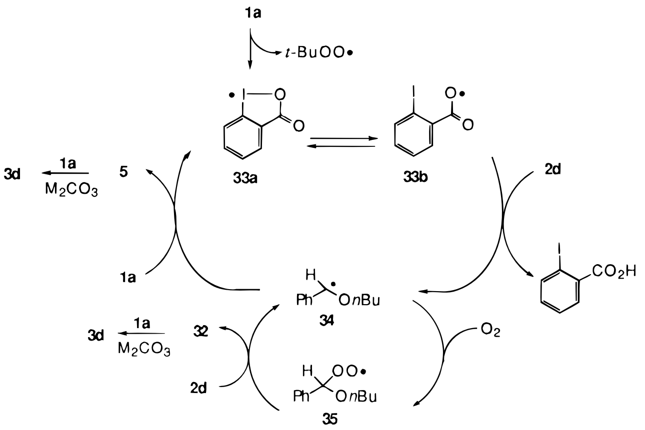
CO_3 or **1a**. Combining K_2CO_3 and **1a** was not found to improve the yield of **3d**.



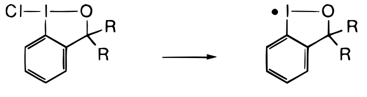
It has been well established that autoxidation of benzyl ethers produces α-hydroperoxybenzyl ethers via the reaction of generated benzyl radicals with dioxygen, and dehydration of the resulting hydroperoxyacetals gives rise to esters.[34,42] The reactions of benzyl radicals with dioxygen are exothermic to the extent of about 13 kcal/mol, and activation energies for the reaction have been estimated to be zero.[43] Therefore, although we have no explicit evidence for the intervention of **32**, it seems most likely that the reaction of **2d** with **1a** under standard conditions, that is, in the presence of oxygen, would produce the hydroperoxy acetal **32** as an intermediate via the reaction of generated benzyl radical with dioxygen. As shown in Table 7, treatment of **32**, prepared by ruthenium(III)-catalyzed acetal exchange of **31** with hydrogen peroxide, with K_2CO_3 and **1a** afforded the ester **3d** in 44% and 66% yields, respectively. These reactivity differences between the peroxy acetal **5** and the hydroperoxy acetal **32** toward K_2CO_3 might be attributed to the higher leaving group ability of the HO group compared to that of the *tert*-BuO group.[44]

Reaction Mechanism. As illustrated in Scheme 1, a reaction mechanism for the benzylic oxidation of **2d** with **1a** might be assumed to involve the following key steps: (a) bond cleavage of the hypervalent iodine(III)−peroxy bond of **1a** generating *tert*-butylperoxy radical and iodanyl (iodinanyl) radical **33a**, (b) benzylic hydrogen abstraction of **2d** with iodanyl radical **33a** or benzoyloxy radical **33b** generating benzylic radical **34**, (c) nucleophilic attack of the benzylic radical **34** to iodine(III)−peroxy bond of **1a** yielding the *tert*-butylperoxy acetal **5** with concomitant regeneration of iodanyl radical **33a**, and (d) decomposition of the *tert*-butylperoxy acetal **5** to produce the ester **3d**. In the presence of dioxygen, the following alternative pathway would also compete: (e) reactions of benzyl radical **34** with dioxygen generating peroxy radical **35**, (f) hydrogen abstraction with the peroxy radical **35** yielding the hydroperoxy acetal **32** with concomitant regeneration of benzyl radical **34**, and (g) decomposition of the hydroperoxy acetal **32** to produce the ester **3d**.

Scheme 1



The radical nature of the oxidation was substantiated by the inhibition of the reaction with added radical scavengers. Rates for decomposition of **1a** were measured spectrophotometrically in dichloromethane at 30 °C. The first-order rate constant $k_{\text{obsd}} = 2.62 \times 10^{-5}\ \text{s}^{-1}$ was obtained, and the half-life of **1a** was about 7.4 h. The major pathway of the decomposition of PhI-$(OOtBu)_2$ at −80 °C has been reported to be the homolytic cleavage of the hypervalent I−O bonds.[4a,45] Furthermore, the unimolecular free radical decomposition of [bis(perbenzoyloxy)-iodo]benzenes has been studied kinetically.[2] Therefore, it seems reasonable to assume that the initial step of the benzylic oxidation would involve the homolytic bond cleavage of the weak iodine(III)−peroxy bond of **1a**, which generates the [9-I-2] iodanyl radical **33a** and *tert*-butylperoxy radical.



36: R = Me, CF_3 **37**

Generation of the iodine-centered radicals from hypervalent iodanes has been shown to be an energetically favorable process, since it involves breaking weak bonds to iodine(III).[46] The intermediacy of electrophilic iodanyl radicals as a highly selective hydrogen-abstracting species has been established in the photoinitiated for thermally initiated chlorination with (dichloroiodo)benzene,[47,48] [chloro(*tert*-butoxy)iodo]benzene,[49] and the Martin's cyclic chloroiodane **36**.[46] For instance, under photochemical conditions, **36** generates the cyclic alkoxyiodanyl radical **37**. Thermolysis and photolysis of (diacyloxyiodo)-

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(42) (a) Sharp, D. B.; Patrick, T. M. *J. Org. Chem.* **1961**, *26*, 1389. (b) Rieche, A.; Schmitz, E. *Chem. Ber.* **1957**, *90*, 1084. (c) Rieche, A.; Seyfarth, H. E.; Brand, F. *Liebigs Ann. Chem.* **1969**, *725*, 93. (d) Schenck, G. O.; Becker, H.-D.; Schulte-Elte, K.-H.; Krauch, C. H. *Chem. Ber.* **1963**, *96*, 509. (e) Milas, N. A.; Peeler, R. L.; Mageli, O. L. *J. Am. Chem. Soc.* **1954**, *76*, 2322. (f) Schreiber, S.; Hulin, B.; Liew, W. *Tetrahedron* **1986**, *42*, 2945.

(43) Howard, J. A. *Free Radicals*; Wiley: New York, 1973; Vol. 2, Chapter 12.

(44) Curci, R.; DiFuria, F. *Tetrahedron Lett.* **1974**, 4085.

(45) The unimolecular free-radical decomposition of [bis(perbenzoyloxy)-iodo]benzenes in chloroform has been reported to involve the homolytic cleavage of the O−O bonds.[2b]

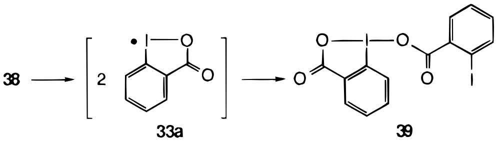
(46) Amey, R. L.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 3060.

(47) (a) Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 4987. (b) Banks, D. F.; Huyser, E. S.; Kleinburg, J. *J. Org. Chem.* **1964**, *29*, 3692. (c) Tanner, D. D.; Bostelen, P. B. *J. Org. Chem.* **1967**, *32*, 1517. (d) Tanner, D. D.; Gidley, G. C. *J. Org. Chem.* **1968**, *33*, 38. (e) Arase, A.; Hoshi, M.; Masuda, Y. *Chem. Lett.* **1979**, 961.

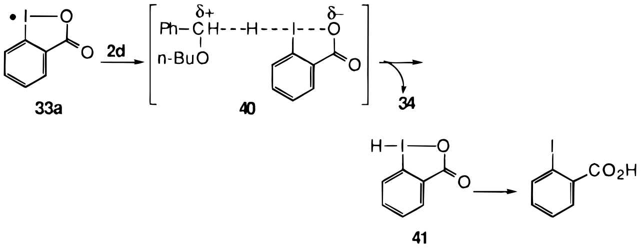
(48) Breslow and his co-workers developed the template-directed chlorination of steroids via generation of iodanyl radicals. See: (a) Breslow, R.; Corcoran, R.; Dale, J. A.; Liu, S.; Kalicky, P. *J. Am. Chem. Soc.* **1974**, *96*, 1973. (b) Breslow, R.; Corcoran, R. J.; Snider, B. B. *J. Am. Chem. Soc.* **1974**, *96*, 6791. (c) Breslow, R.; Snider, B. B.; Corcoran, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 6794. (d) White, P.; Breslow, R. *J. Am. Chem. Soc.* **1990**, *112*, 6842.

(49) Tanner, D. D.; Gidley, G. C. *Can. J. Chem.* **1968**, *46*, 3537.

benzenes also generate [9-I-2] iodanyl radicals.[50] The generation of the iodanyl radical **33a** has been proposed in the iodine-accelerated facile rearrangement of bis(*o*-iodobenzoyl) peroxide **38** to the cyclic iodane **39** in chloroform at 25 °C.[51]

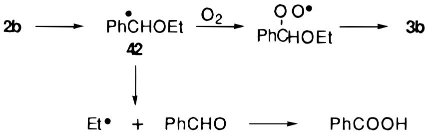


The iodanyl radical **33a** or the benzoyloxy radical **33b** could selectively abstract benzylic α-hydrogens of **2d**, generating the benzyl radical **34**.[52,53] It is very difficult to determine whether benzylic hydrogen abstraction by **33a** occurs at the iodine or at the oxygen attached to iodine.[46] The former process leads to a hydridoiodane **41**, which might rearrange to *o*-iodobenzoic acid, while the latter process gives the acid directly.[54] Both Huyser[47b] and Tanner[47c] have suggested that in chlorination of hydrocarbons the iodanyl radicals such as PhİCl and PhİO*t*Bu abstract hydrogens of hydrocarbons at the iodine. On the other hand, molecular mechanics calculations on template-directed steroid chlorinations, as reported by Breslow,[48] have led to the suggestion that hydrogen abstraction occurs at a chlorine attached to the iodine. The large value of isotope effect ($k_H/k_D = 13$) observed for oxidation of benzyl *n*-butyl ether **2d** shows the high sensitivity of the radical **33a** or **33b** to the bond strength of the breaking C−H, and the relative rates of oxidation of substituted benzyl ethers **2d** and **2p-s** shown in Table 6, where electron-releasing groups such as *p*-MeO and *p*-Me increase the rate of oxidation, indicate the electrophilic nature of **33a** or **33b**. The better Hammett correlation of the oxidation rates of the benzyl ethers with σ^+ implies that there is some separation of charge in the transition state such as **40** for hydrogen abstraction.[55]

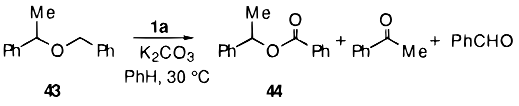


The benzyl radical **34** is then oxidized through a ligand-transfer process[57] by the peroxyiodane **1a**, which produces the *tert*-butylperoxy acetal **5** and regenerates the iodanyl radical **33a**. As discussed above, the TEMPO trapping experiments under argon show that this ligand-transfer process is very rapid, with the estimated rate constant $k \approx 10^8\ \mathrm{M^{-1}\ s^{-1}}$. In the presence of dioxygen, this ligand-transfer process would compete with the reaction of **34** with dioxygen, producing the peroxy radical **35**, which is one of the steps in autoxidation, since the rate constants for dioxygen trapping of benzyl radicals have been estimated to be greater than $10^8\ \mathrm{M^{-1}\ s^{-1}}$.[43]

The benzylic oxidation by **1a** must involve hydrogen abstraction by the iodanyl radical **33a** or benzoyloxy radical **33b**; however, the radical **33a** or **33b** could not be the sole radical that abstracts benzylic hydrogens, since a large amount of the ester **3d** (*ca.* 600%) was formed in the presence of dioxygen (Table 5, entries 15 and 16). Therefore, it seems reasonable to assume that hydrogen abstraction by the peroxy radical **35** generating **34** and the hydroperoxy acetal **32**, which was observed in autoxidation, plays an important role in this oxidation under standard conditions.[58]



Li and Alper have reported that Co(II)-catalyzed oxidation of benzyl ethyl ether (**2b**) with atmospheric oxygen at 80 °C produces a mixture of the ester **3b** (47%) and benzoic acid (50%) via formation of the benzyl radical **42**. They attribute the formation of benzoic acid to the facile fragmentation of the radical **42** to ethyl radical and benzaldehyde which is oxidized to benzoic acid.[20] Here, oxidation of **2b** with **1a** at room temperature gave the ester **3b** selectively, in high yield, and neither benzaldehyde nor benzoic acid was detected (Table 2, entry 2). This result is probably due to the rapid reaction of the benzyl radical **42** with **1a** as well as with dioxygen, and the low reaction temperature. On the other hand, this type of fragmentation of benzyl radicals becomes important when it leads to the generation of very stable radicals. For instance, in the oxidation of benzyl α-methylbenzyl ether **43** with **1a**, significant amounts of fragmentation products, acetophenone (79%) and benzaldehyde (67%), in addition to the normal oxidation product α-methylbenzyl benzoate **44** (20%) were obtained.



An alternative pathway to the formation of the benzyl radicals involves electron transfer which generates benzyl ether cation radicals and the follow-up proton transfer. In fact, oxidation of the benzyl ether protecting group by a stable cation radical derived from tris(*p*-bromophenyl)amine or by electrochemical methods has been shown to involve generation of the benzyl

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(50) (a) Fontana, F.; Minisci, F.; Yan, Y. M.; Zhao, L. *Tetrahedron Lett.* **1993**, *34*, 2517. (b) Wang, T. T.; Leffler, J. E. *J. Org. Chem.* **1971**, *36*, 1531. (c) Cribb, C. J.; Gill, G. B.; El-Jamali, H. A. R. *J. Chem. Soc., Perkin Trans. 2* **1977**, 860. (d) Minisci, F.; Vismara, E.; Fontana, F.; Barbosa, M. C. N. *Tetrahedron Lett.* **1989**, *30*, 4659. (e) Togo, H.; Aoki, M.; Yokoyama, M. *Chem. Lett.* **1991**, 1691. (f) Togo, H.; Aoki, M.; Yokoyama, M. *Tetrahedron Lett.* **1991**, *32*, 6559. (g) Togo, H.; Aoki, M.; Yokoyama, M. *Tetrahedron* **1993**, *49*, 8241.

(51) (a) Leffler, J. E.; Faulkner, R. D.; Petropoulos, C. C. *J. Am. Chem. Soc.* **1958**, *80*, 5435. (b) Honsberg, W.; Leffler, J. E. *J. Org. Chem.* **1961**, *26*, 733. (c) Bentrude, W. G.; Martin, J. C. *J. Am. Chem. Soc.* **1962**, *84*, 1561. (d) Tuleen, D. L.; Bentrude, W. G.; Martin, J. C. *J. Am. Chem. Soc.* **1963**, *85*, 1938.

(52) *tert*-Butylperoxy radical may also abstract benzylic hydrogens of **2d**.

(53) Benzoyloxy radicals have been shown to be easily decarboxylated with a rate constant $2.4 \times 10^4\ \mathrm{s^{-1}}$ at 80 °C;[50c] however, since no formation of iodobenzene was detected in the reactions, the iodanyl radical **33** does not seem to undergo decarboxylation under our standard conditions. This finding may be due to a neighboring group effect of the *o*-iodine, which stabilizes carboxy radicals by resonance.[51]

(54) Benzylic hydrogen abstractions of benzyl ethers by benzoyloxy radical have been studied in detail.[34a] See also: (a) Cass, W. E. *J. Am. Chem. Soc.* **1947**, *69*, 500. (b) Cass, W. E. *J. Am. Chem. Soc.* **1950**, *72*, 4915.

(55) Polar transition states for hydrogen abstraction by ROO•,[34,56] halogen,[34b] and iodanyl radicals[46] have been generally accepted.

(56) (a) Hendry, D. G.; Russell, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 2368. (b) Russell, G. A. *J. Am. Chem. Soc.* **1957**, *79*, 3871. (c) Rust, F. F.; Youngman, E. A. *J. Org. Chem.* **1962**, *27*, 3778.

(57) Minisci, F.; Fontana, F.; Araneo, S.; Recupero, F.; Banfi, S.; Quici, S. *J. Am. Chem. Soc.* **1995**, *117*, 226.

(58) The rate constant for hydrogen abstraction by alkylperoxy radicals has been measured for benzylic ethers, and typically has a value of $6\ \mathrm{M^{-1}\ s^{-1}}$.[43]

ether cation radical via electron transfer.[8,59] The subsequent proton transfer from the cation radical will generate benzyl radicals and be considerably accelerated in the presence of a base such as Na_2CO_3, AcOK, and 2,6-dimethylpyridine.

The addition of alkali metal carbons markedly accelerates the benzyl ether oxidation with **1a**, which suggests an electron transfer−proton transfer mechanism involving the intermediacy of benzyl ether cation radicals. It should be noted, however, that deprotonation of the benzyl methyl ether radical cation in MeCN is exergonic by −15 kcal mol^{-1} and occurs very rapidly.[35b,60] Furthermore, the very large deuterium isotope effect ($k_H/k_D = 12-14$) observed in the reaction of **2d** indicates that the rate-determining step is not an electron-transfer process, a conclusion further supported by the findings that no good correlation was obtained between the relative rates of oxidation of substituted benzyl ethers **2d** and **2p**−**s** (Table 6) and their ionization potentials calculated by the PM3 molecular orbital method.[61] Additional evidence against the single electron transfer mechanism is the observation that peroxyiodane oxidation of **2d**[62] was not retarded in the presence of 1,4-dimethoxybenzene, a single electron transfer quencher with the oxidation potential $E_{ox} = 1.28$ V (vs SCE in MeCN).[63]

The peroxyiodane oxidation of **2d** is sensitive to the nature of solvents. The solvent effects presented in Table 1 indicate that changes in solvent polarity have a great influence on product yields, which increase with decreasing solvent polarity. We obtained a good linear correlation between the yields of **3d** and Dimroth's $E_T(30)$ values.[11] This solvent effect can be attributed to the polar character of the cyclic iodanyl radical **33a** as well as to the alkylperoxy radicals in their ground state. The alkylperoxy radicals have been shown to be π-radicals with large dipole moments.[64,65] These hydrogen abstracting radicals would be more efficiently solvated in polar solvents, which lead to deactivation of these radicals. The reactivity of these radicals is probably reduced by hydrogen bonding with protic solvents.[56]

Conclusion

Compared to other oxidizing reagents such as CrO_3, $PhCH_2N^+Et_3{\cdot}MnO_4^-$, and RuO_4, used for deprotection of benzyl and allyl ethers, the (*tert*-butylperoxy)iodane **1a** is more useful for three reasons: it does not contain poisonous heavy metals, the *o*-iodobenzoic acid formed can be recycled by oxidation to the hypervalent iodane, and the oxidation proceeds under mild conditions, making the reaction compatible with other protecting groups such as MOM, THP, and TBDMS ethers, and acetoxy groups. Oxidation with **1a** occurs readily with C−H bonds activated by both enthalpic effects (benzylic, allylic, and propargylic C−H bonds) and/or polar effects (α-oxy C−H bonds), generating α-oxy carbon-centered radicals. Finally, (*tert*-butylperoxy)iodane **1a**, very stable in the solid state, can generate a *tert*-butylperoxy radical and the iodanyl radical via homolytic bond cleavage of the hypervalent iodine(III)−peroxy bond *even at room temperature* in solution with a first-order rate constant $k_{obsd} = 2.62 \times 10^{-5}\ s^{-1}$ (in CH_2Cl_2).

Experimental Section

General Information. IR spectra were recorded on Jasco IRA-1 and Perkin Elmer 1720 FT-IR spectrometers. ^1H and ^{13}C NMR were recorded in $CDCl_3$ on JEOL JMN-GX 270 and 400 spectrometers. Chemical shifts were reported in parts per million (ppm) downfield from internal Me_4Si. Mass spectra (MS) were obtained on a JEOL JMS-DX300 spectrometer. Melting points were determined with a Yanaco micro melting points apparatus and are uncorrected.

Unless otherwise noted, reactions were performed under nitrogen atmosphere using a rubber balloon. Benzene and cyclohexane were dried over CaH_2 and distilled. BF_3-Et_2O was distilled from CaH_2 under nitrogen. Analytical gas chromatography (GC) was carried out on a Shimadzu GC-14A gas chromatograph with a column of 20% Silicone GE SF-96 on Chromosorb W (AW-DMCS). Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (Merck, silica gel F-254). Kieselgel 60 (Merck, 230−400 mesh) was used for flash chromatography.

Substrates. Benzyl methyl ether (**2a**), phthalan (**2u**), isochroman (**2v**), indan, 5-methoxyindan, tetrahydronaphthalene, and 1-phenylhexane (**18b**) were purchased from Tokyo Kasei Kogyo Co. and distilled prior to use. Diphenylmethane, 9,10-dihydroanthracene, anthrone, xanthene, and fluorene (**18a**) are commercially available. Other benzyl ethers were prepared by the reaction of sodium alkoxides with benzyl bromide in the presence of tetrabutylammonium iodide.[66] Benzyl ethers prepared by this way and their ^1H NMR are as follows: benzyl ethyl ether (**2b**),[67] δ 7.35−7.28 (m, 5H), 4.50 (s, 2 H), 3.53 (q, $J = 6.4$ Hz, 2 H), 1.24 (t, $J = 6.4$ Hz, 3 H); benzyl 2-propyl ether (**2c**),[68] δ 7.34−7.28 (m, 5 H), 4.50 (s, 2 H), 3.67 (sept, $J = 6.1$ Hz, 1 H), 1.21 (d, $J = 6.1$ Hz, 6 H); benzyl *n*-butyl ether (**2d**),[9d] δ 7.33 (m, 5 H), 4.50 (s, 2 H), 3.47 (t, $J = 6.5$ Hz, 2 H), 1.67−1.31 (m, 4 H), 0.92 (t, $J = 7.3$ Hz, 3 H); benzyl 2-butyl ether (**2e**),[69] δ 7.33 (m, 5 H), 4.56 (d, $J = 11.7$ Hz, 1 H), 4.46 (d, $J = 11.7$ Hz, 1 H), 3.44 (sext, $J = 6.1$ Hz, 1 H), 1.81−1.43 (m, 2 H), 1.18 (d, $J = 6.1$ Hz, 3 H), 0.93 (t, $J = 6.4$ Hz, 3 H); benzyl *tert*-butyl ether (**2f**),[9a,70] δ 7.40−7.20 (m, 5 H), 4.45 (s, 2 H), 1.29 (s, 9 H); benzyl cyclopentyl ether (**2g**),[9b] δ 7.31 (m, 5 H), 4.47 (s, 2 H), 4.06−3.88 (m, 1 H), 1.80−1.39 (m, 8 H); benzyl cyclohexyl ether (**2h**),[9a,70] δ 7.30 (m, 5 H), 4.53 (s, 2 H), 3.43−3.24 (m, 1 H), 2.00−1.17 (m, 10 H); benzyl 1-methylcyclohexyl ether (**2i**), δ 7.40−7.21 (m, 5 H), 4.41 (s, 2 H), 1.90−1.20 (m, 10 H), 1.22 (s, 3 H); benzyl menthyl ether (**2j**),[9c] δ 7.33 (m, 5 H), 4.66 (d, $J = 11.5$ Hz, 1 H), 4.39 (d, $J = 11.5$ Hz, 1 H), 3.17 (dt, $J = 4.2$, 10.5 Hz, 1 H), 2.43−2.12 (m, 2 H), 1.80−0.90 (m, 7 H), 0.93 (d, $J = 7.3$ Hz, 3 H), 0.90 (d, $J = 7.3$ Hz, 3 H), 0.70 (d, $J = 6.8$ Hz, 3 H); benzyl *cis*-4-*tert*-butylcyclohexyl ether (**2k**), δ 7.40−7.18 (m, 5 H), 4.50 (s, 2 H), 3.68−3.56 (m, 1 H), 2.08−1.92 (m, 2 H), 1.60−1.20 (m, 7 H), 0.86 (s, 9 H); benzyl *trans*-4-*tert*-butylcyclohexyl ether (**2l**), δ 7.40−7.17 (m, 5 H), 4.55 (s, 2 H), 3.25 (tt, $J = 11.0$, 4.4 Hz, 1 H), 2.20−2.04 (m, 2 H), 1.87−1.72 (m, 2 H), 1.40−0.90 (m, 5 H), 0.84 (s, 9 H); benzyl *cis*-2-methylcyclohexyl ether (**2m**), δ 7.46−7.18 (m, 5 H), 4.58 (d, $J = 12.2$ Hz, 1 H), 4.43 (d, $J = 12.2$ Hz, 1 H), 3.44 (dt, $J = 6.1$, 3.0 Hz, 1 H), 1.97−1.12 (m, 9 H), 0.97 (d, $J = 7.1$ Hz, 3 H); benzyl *trans*-2-methylcyclohexyl ether (**2n**), δ 7.46−7.18 (m, 5 H), 4.64 (d, $J = 11.7$ Hz, 1 H), 4.43 (d, $J = 11.7$ Hz, 1 H), 2.90 (dt, $J = 4.5$, 9.5 Hz, 1 H), 2.30−2.00 (m, 1 H), 1.89−1.09 (m, 8 H), 1.02 (d, $J = 6.4$ Hz,

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(59) Photoelectron spectroscopy shows that the oxidation potential of aromatic π electrons of benzyl ethers is lower than that of the nonbonding electrons on oxygen. Therefore, the charge density of benzyl ether cation radicals has been assumed to be located in the π system rather than localized on the potentially oxidizable oxygen atom. See: (a) Mayeda, E. A.; Miller, L. L.; Wolf, J. F. *J. Am. Chem. Soc.* **1972**, *94*, 6812. (b) Pincock, J. A.; Pincock, A. L.; Fox, M. A. *Tetrahedron* **1985**, *41*, 4107.

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3 H); benzyl phenyl ether (**2o**),[9a,70] δ 7.47−7.19 (m, 7 H), 7.00−6.88 (3 H), 5.04 (s, 2 H); *n*-butyl *p*-methoxybenzyl ether (**2p**),[71] δ 7.25 (dt, J = 8.5, 2.2 Hz, 2 H), 6.86 (dt, J = 8.5, 2.2 Hz, 2 H), 4.42 (s, 2 H), 3.79 (s, 3 H), 3.44 (t, J = 6.5 Hz, 2 H), 1.64−1.30 (m, 4 H), 0.91 (t, J = 7.2 Hz, 3 H); *n*-butyl *p*-methylbenzyl ether (**2q**),[72] δ 7.22 (d, J = 8.1 Hz, 2 H), 7.13 (d, J = 8.1 Hz, 2 H), 4.46 (s, 2 H), 3.45 (t, J = 6.6 Hz, 2 H), 2.33 (s, 3 H), 1.66−1.25 (m, 4 H), 0.91 (t, J = 7.1 Hz, 3 H); *n*-butyl *p*-chlorobenzyl ether (**2r**),[71] δ 7.28 (m, 4 H), 4.45 (s, 2 H), 3.46 (t, J = 6.5 Hz, 2 H), 1.63−1.37 (m, 4 H), 0.92 (t, J = 7.2 Hz, 3 H); *n*-butyl *m*-clorobenzyl ether (**2s**),[71] δ 7.33 (br s, 1 H), 7.25 (m, 3 H), 4.46 (s, 2 H), 3.47 (t, J = 6.3 Hz, 2 H), 1.67−1.22 (m, 4 H), 0.92 (t, J = 7.6 Hz, 3 H); *n*-butyl *p*-phenylbenzyl ether (**2t**), δ 7.66−7.50 (m, 4 H), 7.50−7.26 (m, 5 H), 4.52 (s, 2 H), 3.49 (t, J = 6.5 Hz, 2 H), 1.69−1.31 (m, 4 H), 0.92 (t, J = 7.1 Hz, 3 H); benzyl 3β-cholesteryl ether (**21c**), δ 7.44−7.20 (m, 5 H), 5.33 (m, 1 H), 4.56 (s, 2 H), 3.38−3.14 (m, 1 H), 2.51−2.16 (m, 2 H), 2.12−1.72 (m, 5 H), 1.72−0.76 (m, 21 H), 1.01 (s, 3 H), 0.91 (d, J = 6.6 Hz, 3 H), 0.86 (d, J = 6.6 Hz, 6 H), 0.68 (s, 3 H); benzyl 3-butenyl ether (**23**),[73] δ 7.73 (m, 5 H), 5.84 (ddt, J = 17.1, 10.0, 6.5 Hz, 1 H), 5.12 (br d, J = 17.1 Hz, 1 H), 5.08 (br d, J = 10.0 Hz, 1 H), 4.53 (s, 2 H), 3.53 (t, J = 6.8 Hz, 2 H), 2.38 (br q, J = 6.6 Hz, 2 H); benzyl α-methylbenzyl ether (**43**), δ 7.33 (m, 10 H), 4.50 (q, J = 6.5 Hz, 1 H), 4.45 (d, J = 11.7 Hz, 1 H), 4.29 (d, J = 11.7 Hz, 1 H), 1.48 (d, J = 6.5 Hz, 3 H).

1-(Benzyloxy)-5-(methoxymethoxy)-3-methylpentane (2w): 1-(Benzyloxy)-5-hydroxy-3-methylpentane was prepared by reaction of the sodium alkoxide of 1,5-dihydroxy-3-methylpentane with benzyl bromide in the presence of tetrabutylammonium iodide in 73% yield.[66] To a stirred suspension of sodium hydride (96 mg, 2.4 mmol) in tetrahydrofuran (5 mL) were added dropwise 1-(benzyloxy)-5-hydroxy-3-methylpentane (500 mg, 2.4 mmol) and chloromethyl methyl ether (231 mg, 2.87 mmol) under nitrogen at room temperature, and stirring was continued for 21 h. The mixture was poured over ice and extracted with diethyl ether, and the organic phase was washed with brine. The solution was dried over anhydrous Na_2SO_4 and concentrated. Flash chromatography of the crude product mixture yielded **2w** (313 mg, 49%): colorless oil; IR ($CHCl_3$) 2928, 1455, 1366, 1109, 1040, 737, 698 cm^{-1}; ^1H NMR δ 7.33 (m, 5 H), 4.61 (s, 2 H), 4.50 (s, 2 H), 3.62−3.44 (4 H), 3.35 (s, 3 H), 1.88−1.28 (m, 5 H), 0.92 (d, J = 6.4 Hz, 3 H); MS *m*/*z* (rel intensity) 253 (1, $M^+ + 1$), 131 (5), 110 (30), 94 (100), 81 (59), 66 (100), 51 (45); HRMS, calcd for $C_{15}H_{25}O_3$ ($M^+ + 1$) 253.1804, found 253.1844.

1-(Benzyloxy)-3-methyl-5-(tetrahydropyranoxy)pentane (2x): To a solution of 1-(benzyloxy)-5-hydroxy-3-methylpentane (300 mg, 1.40 mmol) and 3,4-dihydro-2*H*-pyran (639 mg, 7.17 mmol) in dichloromethane (15 mL) was added *p*-toluenesulfonic acid (3.0 g, 16.8 mmol) under nitrogen at room temperature, and the mixture was stirred for 27 h. The mixture was poured over ice and extracted with diethyl ether, and the organic phase was washed with brine. The solution was dried over anhydrous Na_2SO_4 and concentrated. Flash chromatography of the crude product mixture yielded **2x** (264 mg, 62%): colorless oil; ^1H NMR δ 7.32 (m, 5 H), 4.57 (m, 1 H), 4.50 (s, 2 H), 4.00−3.68 (m, 2 H), 3.60−3.28 (m, 4 H), 1.96−1.28 (m, 11 H), 0.92 (d, J = 6.4 Hz, 3 H); MS *m*/*z* (rel intensity) 207 (11, $M^+ - C_5H_9O$), 191 (9), 185 (7), 105 (100), 101 (72), 83 (67), 67 (34), 55 (73); HRMS, calcd for $C_{13}H_{19}O_2$ ($M^+ - C_5H_9O$) 207.1385, found 207.1372.

1-(Benzyloxy)-5-(*tert*-butyldimethylsiloxy)-3-methylpentane (2y): To a solution of 1-(benzyloxy)-5-hydroxy-3-methylpentane (500 mg, 2.4 mmol) and imidazole (570 mg, 8.4 mmol) in *N*,*N*-dimethylformamide (2 mL) was added *tert*-butyldimethylchlorosilane (432 mg, 2.87 mmol) under nitrogen at room temperature, and the mixture was stirred for 5 h. The mixture was poured over ice and extracted with diethyl ether, and the organic phase was washed with brine. The solution was dried over anhydrous Na_2SO_4 and concentrated. Flash chromatography of the crude product mixture yielded **2y** (756 mg, 98%): colorless oil; IR ($CHCl_3$) 2929, 2857, 1463, 1255, 1098, 836, 776, 734, 697 cm^{-1}; ^1H NMR δ 7.33 (m, 5 H), 4.50 (s, 2 H), 3.66 (dt, J = 1.2, 6.8 Hz, 2 H), 3.53 (t, J = 6.8 Hz, 2 H), 1.84−1.24 (m, 5 H), 0.91 (d, J = 6.4 Hz, 3 H), 0.90 (s, 9 H), 0.05 (s, 6 H); MS *m*/*z* (rel intensity) 265 (3, $M^+ - C_4H_9$), 173 (56), 143 (25), 92 (100), 75 (54); HRMS, calcd for $C_{15}H_{25}O_2Si$ ($M^+ - C_4H_9$) 265.1624, found 265.1585.

5-Acetoxy-1-(benzyloxy)-3-methylpentane (2z): To a solution of 1-(benzyloxy)-5-hydroxy-3-methylpentane (462 mg, 2.21 mmol) in pyridine (21 mL) was added acetic anhydride (2.4 g, 24 mmol) under nitrogen at 0 °C, and the solution was stirred for 0.5 h. After evaporation in vacuo, flash chromatography yielded **2z** (375 mg, 64%): colorless oil; IR ($CHCl_3$) 2929, 1740, 1455, 1367, 1240, 1101, 738, 699 cm^{-1}; ^1H NMR δ 7.32 (m, 5 H), 4.49 (s, 2 H), 4.10 (dt, J = 6.6, 1.3 Hz, 2 H), 3.51 (t, J = 6.5 Hz, 2 H), 2.03 (s, 3 H), 1.84−1.32 (m, 5 H), 0.92 (d, J = 6.4 Hz, 3 H); MS *m*/*z* (rel intensity) 250 (8, M^+), 190 (16), 133 (16), 107 (97), 92 (55), 61 (100), 43 (93); HRMS, calcd for $C_{15}H_{22}O_3$ (M^+) 250.1569, found 250.1569.

Benzyl 4,4-Diphenyl-3-butenyl Ether (26): A mixture of sodium 4-hydroxybutanoate (126 mg, 1.00 mmol) and sodium hydride (24 mg, 1.0 mmol, 60% dispersion in oil) in *N*,*N*-dimethylformamide (10 mL) was stirred under nitrogen at room temperature for 1 h. Benzyl bromide (429 mg, 2.50 mmol) was added, and the mixture was stirred for 25 h. The mixture was poured into water and extracted with diethyl ether. The organic phase was washed with brine and dried over anhydrous Na_2SO_4 and concentrated. Chromatography of the crude mixture yielded benzyl 4-(benzyloxy)butanoate (61 mg, 21%): IR (film) 3032, 2860, 1735, 1455, 1166, 1106, 738, 698 cm^{-1}; ^1H NMR δ 7.34 (s, 5 H), 7.31 (s, 5 H), 5.10 (s, 2 H), 4.47 (s, 2 H), 3.50 (t, J = 6.3 Hz, 2 H), 2.49 (t, J = 7.2 Hz, 2 H), 1.96 (br quint, J = 6.7 Hz, 2 H). To a solution of benzyl 4-(benzyloxy)butanoate (90 mg, 0.32 mmol) in tetrahydrofuran (10 mL) was added dropwise a tetrahydrofuran solution of phenylmagnesium bromide (2 M solution, 0.47 mL, 0.96 mmol) under nitrogen at room temperature, and the mixture was heated at reflux for 16 h. The mixture was quenched with water, acidified with 5% aqueous HCl, and extracted with dichloromethane. The organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Chromatography of the crude mixture yielded 4-(benzyloxy)-1,1-diphenylbutanol (57 mg, 55%): pale yellow oil; IR (film) 3423, 3029, 2862, 1494, 1449, 1363, 1102, 747, 699 cm^{-1}; ^1H NMR δ 7.45−7.19 (m, 15 H), 4.47 (s, 2 H), 3.50 (t, J = 6.0 Hz, 2 H), 3.39 (s, 1 H), 2.42 (t, J = 7.2 Hz, 2 H), 1.65 (m, 2 H). A mixture of 4-(benzyloxy)-1,1-diphenylbutanol (7.9 mg, 0.024 mmol) and *p*-toluenesulfonic acid (1.0 mg) in benzene (1 mL) was heated at reflux for 1 min. The mixture was poured into water and extracted with dichloromethane. The organic phase was washed with brine, dried with anhydrous Na_2SO_4, and concentrated. Preparative TLC of the crude product mixture yielded (**26**) (5.5 mg, 74%):[74] pale yellow oil; IR (film) 3028, 2856, 1495, 1445, 1362, 1099, 1029, 770, 698 cm^{-1}; ^1H NMR δ 7.37−7.16 (m, 15 H), 6.14 (t, J = 7.0 Hz, 1 H), 4.50 (s, 2 H), 3.56 (t, J = 7.0 Hz, 2 H), 2.45 (q, J = 7.0 Hz, 2 H).

Allyl and propargyl ethers were prepared by the reaction of sodium alkoxides with 2-propenyl, 2-methyl-2-propenyl, 3-methyl-2-butenyl, *trans*-cinnamyl, propargyl, and 2-butynyl bromides in the presence of tetrabutylammonium iodide.[66] Allyl and propargyl ethers prepared by this way and their ^1H NMR are as follows: allyl *n*-decyl ether (**6a**),[75] δ 5.92 (ddt, J = 17.1, 10.5, 5.5 Hz, 1 H), 5.26 (br d, J = 17.1 Hz, 1 H), 5.16 (br d, J = 10.5 Hz, 1 H), 3.96 (br d, J = 5.5 Hz, 2 H), 3.42 (t, J = 6.6 Hz, 2 H), 1.70−1.50 (m, 2 H), 1.42−1.16 (14 H), 0.88 (t, J = 6.4 Hz, 3 H); allyl 2-phenylethyl ether (**6b**),[76] δ 7.41−7.13 (m, 1 H), 5.91 (ddt, J = 17.1, 10.3, 5.6 Hz, 1 H), 5.25 (br d, J = 17.1 Hz, 1 H), 5.16 (br d, J = 10.3 Hz, 1 H), 3.99 (d, J = 5.6 Hz, 2 H), 3.65 (t, J = 7.2 Hz, 2 H), 2.91 (t, J = 7.2 Hz, 2 H); allyl 4-decyl ether (**6c**), δ 5.93 (ddt, J = 17.3, 10.5, 5.6 Hz, 1 H), 5.25 (dq, J = 17.3, 1.5 Hz, 1 H), 5.13 (br d, J = 10.5 Hz, 1 H), 3.97 (dt, J = 5.6, 1.5 Hz, 2 H), 3.28 (quint, J = 6.1 Hz, 1 H), 1.60−1.16 (14 H), 0.91 (t, J = 6.8 Hz, 3 H), 0.88 (t, J = 6.5 Hz, 3 H); allyl 3β-cholestanyl ether (**6d**),[77] δ 5.92 (ddt, J = 17.3, 10.3, 5.6 Hz, 1 H), 5.26 (br d, J = 17.3 Hz, 1 H), 5.14 (br d, J = 10.3 Hz, 1 H), 4.01 (d, J = 5.6 Hz, 2 H), 3.40−3.10 (m, 1 H), 2.08−0.70 (m, 31 H), 0.90 (d, J = 6.8 Hz, 3 H), 0.86 (d, J = 6.6 Hz, 6 H), 0.80 (s, 3 H), 0.65 (s, 3 H); allyl menthyl ether (**6e**),[75] δ 5.93 (ddt, J = 17.1, 10.0, 5.6 Hz, 1 H), 5.26 (br d, J = 17.1 Hz, 1 H), 5.13 (br d, J = 10.0 Hz, 1 H), 4.12 (dd, J = 12.5, 5.6 Hz, 1 H), 3.88 (dd, J = 12.5, 5.6 Hz, 1 H), 3.08 (dt, J = 4.2, 10.5 Hz, 1 H),

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2.42−1.91 (m, 2 H), 1.78−1.48 (m, 2 H), 1.48−1.10 (m, 2 H), 1.10−0.90 (m, 3 H), 0.92 (d, J = 6.4 Hz, 3 H), 0.89 (d, J = 6.8 Hz, 3 H), 0.77 (d, J = 6.8 Hz, 3 H); 1-adamantyl allyl ether (**6f**),[78] δ 5.93 (ddt, J = 17.4, 10.3, 5.0 Hz, 1 H), 5.26 (br d, J = 17.4 Hz, 1 H), 5.12 (br d, J = 10.3 Hz, 1 H), 3.99 (br d, J = 5.0 Hz, 2 H), 2.15 (m, 3 H), 1.82−1.51 (m, 12 H); allyl 4-*tert*-butylphenyl ether (**6g**),[79] δ 7.29 (d, J = 8.7 Hz, 2 H), 6.85 (d, J = 8.7 Hz, 2 H), 6.06 (ddt, J = 17.3, 10.5, 5.1 Hz, 1 H), 5.40 (br d, J = 17.3 Hz, 1 H), 5.27 (br d, J = 10.5 Hz, 1 H), 4.51 (br d, J = 5.1 Hz, 1 H), 1.29 (s, 9 H); *n*-decyl 2-methyl-2-propenyl ether (**8**), δ 4.95 (s, 1 H), 4.88 (s, 1 H), 3.86 (s, 2 H), 3.39 (t, J = 6.4 Hz, 2 H), 1.74 (s, 3 H), 1.70−1.46 (m, 2 H), 1.46−1.10 (14 H), 0.88 (t, J = 6.4 Hz, 3 H); *n*-decyl 3-methyl-2-butenyl ether (**10a**), δ 5.36 (br t, J = 6.8 Hz, 1 H), 3.94 (d, J = 6.8 Hz, 2 H), 3.40 (t, J = 6.6 Hz, 2 H), 1.74 (s, 3 H), 1.67 (s, 3 H), 1.69−1.45 (m, 2 H), 1.45−1.13 (14 H), 0.88 (t, J = 6.4 Hz, 3 H); 3-methyl-2-butenyl-2-phenylethyl ether (**10b**), δ 7.44−7.13 (m, 5 H), 5.35 (br t, J = 6.8 Hz, 1 H), 3.98 (d, J = 6.8 Hz, 2 H), 3.63 (t, J = 7.3 Hz, 2 H), 2.90 (t, J = 7.3 Hz, 2 H), 1.74 (s, 3 H), 1.66 (s, 3 H), menthyl 3-methyl-2-butenyl ether (**10c**), δ 5.35 (br t, J = 6.8 Hz, 1 H), 4.10 (dd, J = 10.8, 6.8 Hz, 1 H), 3.84 (dd, J = 10.8, 6.8 Hz, 1 H), 3.04 (dt, J = 4.2, 10.5 Hz, 1 H), 2.32−2.00 (m, 2 H), 1.74 (s, 3 H), 1.67 (s, 3 H), 1.48−0.9 (m, 7 H), 0.92 (d, J = 6.6 Hz, 3 H), 0.90 (d, J = 7.1 Hz, 3 H), 0.77 (d, J = 6.8 Hz, 3 H); *n*-decyl *trans*-cinnamyl ether (**12**), δ 7.41−7.17 (m, 5 H), 6.60 (br d, J = 15.9 Hz, 1 H), 6.29 (dt, J = 15.9, 5.9 Hz, 1 H), 4.12 (dd, J = 5.9, 1.2 Hz, 2 H), 3.47 (t, J = 6.6 Hz, 2 H), 1.71−1.48 (m, 2 H), 1.48−1.12 (14 H), 0.88 (t, J = 6.3 Hz, 3 H); *n*-decyl propargyl ether (**14a**),[80] δ 4.13 (d, J = 2.3 Hz, 2 H), 3.51 (t, J = 6.3 Hz, 2 H), 2.41 (t, J = 2.3 Hz, 1 H), 1.72−1.46 (m, 2 H), 1.46−1.10 (14 H), 0.88 (t, J = 6.4 Hz, 3 H); *n*-decyl 2-pentynyl ether (**14b**), δ 4.10 (t, J = 2.0 Hz, 2 H), 3.47 (t, J = 6.7 Hz, 2 H), 2.23 (tq, J = 2.0, 7.5 Hz, 2 H), 1.70−1.10 (m, 16 H), 1.14 (t, J = 7.5 Hz, 3 H), 0.88 (t, J = 6.2 Hz, 3 H); *n*-decyl 3-(trimethylsilyl)-2-propynyl ether (**14c**), δ 4.12 (s, 2 H), 3.48 (t, J = 6.6 Hz, 2 H), 1.71−1.44 (m, 2 H), 1.44−1.10 (m, 14 H), 0.87 (t, J = 6.6 Hz, 3 H), 0.16 (s, 9 H); 1-(allyloxy)-5-(benzyloxy)-3-methylpentane (**16a**), δ 7.58−7.12 (m, 5 H), 5.91 (ddt, J = 17.0, 10.3, 5.6 Hz, 1 H), 5.26 (br d, J = 17.0 Hz, 1 H), 5.16 (br d, J = 10.3, 1 H), 4.49 (s, 2 H), 3.95 (br d, J = 5.6, 2 H), 3.51 (t, J = 6.8 Hz, 2 H), 3.46 (t, J = 6.3 Hz, 2 H), 1.94−1.16 (m, 5 H), 0.91 (d, J = 6.4 Hz, 3 H); 5-(benzyloxy)-3-methyl-1-(3-methyl-2-butenyloxy)pentane (**17a**), δ 7.56−7.16 (m, 5 H), 5.35 (br t, J = 6.8 Hz, 1 H), 4.49 (s, 2 H), 3.93 (d, J = 6.8, 2 H), 3.51 (t, J = 6.6 Hz, 2 H), 3.44 (t, J = 6.6 Hz, 2 H), 2.04−1.20 (m, 5 H), 1.74 (s, 3 H), 1.67 (s, 3 H), 0.91 (d, J = 6.1 Hz, 3 H).

Synthesis of 1-(*tert*-Butylperoxy)-1,2-benziodoxol-3(1*H*)-one (1a). To a stirred suspension of commercially available and finely powdered 1-hydroxy-1,2-benziodoxol-3(1*H*)-one (5.53 g, 21.0 mmol) and *tert*-butyl hydroperoxide (3.90 mL of 80% solution in di-*tert*-butyl peroxide, 31.4 mmol) in 60 mL of chloroform was added dropwise BF_3-Et_2O (2.58 mL, 21.0 mmol) at 0 °C under nitrogen, and the mixture was stirred for 3 h. The reaction mixture was quenched with water and the resulting precipitate was removed by filtration. The mixture was extracted with dichloromethane. The extract was washed with water, dried over Na_2SO_4, and concentrated in vacuo to give the peroxyiodane **1a**. Recrystallization from hexane−dichloromethane gave colorless plates (6.33 g, 90%): mp 128.5−129 °C dec; IR ($CHCl_3$) 3030, 3010, 1680, 1600, 1580, 1445, 1370, 1290, 1250, 1190, 1135, 1030, 835 cm^{-1}; ^{1}H NMR δ 8.26 (dd, J = 7.7, 1.5 Hz, 1 H), 8.12 (dd, J = 8.2, 1.0 Hz, 1 H), 7.93 (ddd, J = 8.2, 7.7, 1.5 Hz, 1 H), 7.71 (dt, J = 1.0, 7.7 Hz, 1 H), 1.33 (s, 9 H); ^{13}C NMR δ 167.9, 135.2, 132.3, 130.9, 129.7, 127.5, 120.1, 83.1, 25.9; MS *m/z* (rel intensity) 330 (83), 248 (100), 231 (64), 203 (57), 76 (91). Anal. Calcd for $C_{11}H_{13}IO_4$: C, 39.31; H, 3.90. Found: C, 39.35; H, 3.96.

Synthesis of 1-(*tert*-Butylperoxy)-5-nitro-1,2-benziodoxol-3(1*H*)-one (1b). To a stirred suspension of powdered 1-hydroxy-5-nitro-1,2-benziodoxol-3(1*H*)-one (5.56 g, 18.0 mmol), prepared from 2-iodobenzoic acid by the reaction with concentrated sulfuric acid and fuming nitric acid,[14] and *tert*-butyl hydroperoxide (3.38 mL of 80% solution in di-*tert*-butyl peroxide, 27.0 mmol) in 100 mL of chloroform was added dropwise BF_3-Et_2O (2.22 mL, 18.0 mmol) at room temperature under nitrogen, and the mixture was stirred for 3.5 h. The reaction mixture was quenched with water, and the resulting precipitate was removed by filtration. The mixture was extracted with dichloromethane. The extract was washed with 1% aqueous Na_2CO_3 and water, dried over Na_2SO_4, and concentrated in vacuo to give the peroxyiodane **1b**. Recrystallization from methanol−dichloromethane gave colorless needles (2.79 g, 41%): mp 131−133 °C dec; IR ($CHCl_3$) 2970, 1695, 1675, 1610, 1575, 1535, 1375, 1350, 1260, 1150 cm^{-1}; ^{1}H NMR δ 9.03 (d, J = 2.4 Hz, 1 H), 8.72 (dd, J = 8.8, 2.4 Hz, 1 H), 8.36 (d, J = 8.8 Hz, 1 H), 1.35 (s, 9 H); ^{13}C NMR δ 165.5, 150.9, 132.0, 129.1, 127.0, 126.2, 84.0, 26.0; MS *m/z* (rel intensity) 293 (100), 276 (21), 92 (38), 75 (46), 57 (89), 43 (91). Anal. Calcd for $C_{11}H_{12}INO_6$: C, 34.66; H, 3.17; N, 3.68. Found: C, 34.30; H, 3.14; N, 3.33.

Solvent Effects for Oxidation of Benzyl *n*-Butyl Ether (2d) to *n*-Butyl Benzoate (3d). To a stirred mixture of the peroxyiodane **1a** (148 mg, 0.44 mmol) in an appropriate solvent (4 mL) was added benzyl *n*-butyl ether (**2d**) (33 mg, 0.20 mmol) under nitrogen using a rubber balloon at room temperature, and the mixture was stirred for the periods shown in Table 1. The yield of the benzoate **3d** was determined by gas chromatography using *n*-tridecane as an internal standard and is shown in Table 1. The authentic sample of **3d** was prepared by the reaction of 1-butanol with benzoyl chloride. **3d**:[9d] colorless oil; IR (film) 2961, 2874, 1719, 1452, 1315, 1277, 1177, 1112, 1071, 1028, 711 cm^{-1}; ^{1}H NMR δ 8.04 (br d, J = 8.3 Hz, 2 H), 7.64−7.38 (m, 3 H), 4.33 (t, J = 6.5 Hz, 2 H), 1.83−1.40 (m, 4 H), 0.98 (t, J = 7.3 Hz, 3 H); MS *m/z* (rel intensity) 178 (3, M$^+$), 167 (37), 149 (100), 123 (57), 105 (79), 77 (41), 71 (25), 57 (40).

Reaction of the Peroxyiodane 1a with Methanol. A solution of the peroxyiodane **1a** (34 mg, 0.1 mmol) in methanol (1 mL) was stirred at room temperature for 2 days under nitrogen. After evaporation of the solvent, the residue was dissolved in dichloromethane. The insoluble precipitate was filtered off and washed with dichloromethane. Concentration in vacuo gave 1-methoxy-1,2-benziodoxol-3(1*H*)-one (**4**)[81] (13.9 mg, 50%) as colorless plates: mp 168−170 °C (recrystallized from methanol); IR (KBr) 3083, 1640, 1566, 1442, 1292, 966, 831, 744 cm^{-1}; ^{1}H NMR δ 8.29 (dd, J = 7.6, 1.7 Hz, 1 H), 7.91 (ddd, J = 8.3, 7.6, 1.7 Hz, 1 H), 7.77 (br d, J = 8.3 Hz, 1 H), 7.71 (br dd, J = 8.3, 7.6 Hz, 1 H), 4.28 (s, 3 H); MZ *m/z* (rel intensity) 278 (M$^+$), 248 (100), 231 (68), 203 (56), 76 (76), 50 (42).

Time Courses for Oxidation of the Ether 2d to *n*-Butyl Benzoate (3d). To a stirred mixture of the peroxyiodane **1a** and an appropriate alkali metal carbonate in benzene (5 mL) was added benzyl *n*-butyl ether (**2d**) (33 mg, 0.20 mmol) under nitrogen using a rubber balloon. The mixture was stirred under the conditions described in Figures 1 and 2. As an internal standard, *n*-tridecane was added, and the time course for the reaction was determined by gas chromatography.

General Procedure for Benzylic Oxidation of Benzyl Ethers 2 with the Peroxyiodane 1a. To a stirred mixture of the peroxyiodane **1a** (135 mg, 0.40 mmol) and potassium carbonate (111 mg, 0.80 mmol) in benzene (5 mL) was added a benzyl ether **2** (0.20 mmol) under nitrogen using a rubber balloon at room temperature, and the mixture was stirred for the periods shown in Table 2. The resulting precipitate, which contains potassium salt of *o*-iodobenzoic acid and potassium carbonate, was filtered off and washed with dichloromethane several times. Concentration in vacuo gave an oil, which was purified by preparative TLC. The yields of pure products are given in Table 2. In some experiments, yields were determined by gas chromatography.

***n*-Butyl α-(*tert*-Butylperoxy)benzyl Ether (5):** Colorless oil; IR (film) 2961, 2934, 1364, 1198, 1100, 1003, 754, 698 cm^{-1}; ^{1}H NMR δ 7.61 (br d, J = 7.6 Hz, 2 H), 7.19−7.07 (m, 3 H), 5.91 (s, 1 H), 4.09 (dt, J = 9.5, 6.7 Hz, 1 H), 3.64 (dt, J = 9.5, 6.1 Hz, 1 H), 1.60 (m, 2 H), 1.41 (m, 2 H), 1.21 (s, 9 H), 0.86 (t, J = 7.3 Hz, 3 H); ^{13}C NMR δ 136.9, 128.7, 128.1, 126.9, 106.0, 80.7, 69.3, 32.0, 26.5, 19.3, 13.8; MS *m/z* (rel intensity) 251 (M$^+$ − 1), 179 (41), 163 (100), 108 (100); HRMS, calcd for $C_{11}H_{15}O_3$ (M$^+$ − Bu) 195.1020, found 195.0979. Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.31; H, 9.82.

Oxidative Deprotection of Benzyl Menthyl Ether (2j). To a stirred mixture of the peroxyiodane **1a** (202 mg, 0.60 mmol) and potassium carbonate (166 mg, 1.20 mmol) in benzene (5 mL) was added the benzyl ether **2j** (74 mg, 0.30 mmol) under nitrogen using a rubber balloon at room temperature, and the mixture was stirred for 36 h. After

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evaporation of the solvent in vacuo and addition of a solution of KOH (500 mg, 9.0 mmol) in methanol (5.4 mL) and water (1.3 mL), the mixture was stirred for 17 h at room temperature under nitrogen. The mixture was poured into an aqueous solution of $Na_2S_2O_3$ and extracted with dichloromethane, and the organic phase was washed with brine. The solution was dried over anhydrous Na_2SO_4 and concentrated. Flash chromatography of the crude product yielded 1-menthol (39 mg, 82%) as colorless needles: mp 41−42 °C.

General Procedure for Allylic Oxidation of Allyl Ethers with the Peroxyiodane 1a. To a stirred mixture of the peroxyiodane **1a** (135 mg, 0.40 mmol) and cesium carbonate (130 mg, 0.40 mmol) in cyclohexane (5 mL) was added an allyl ether (0.20 mmol) under an atmosphere at room temperature, and the mixture was stirred for the periods shown in Table 3. The resulting precipitate, which contains cesium salt of *o*-iodobenzoic acid and cesium carbonate, was filtered off and washed with dichloromethane several times. Concentration in vacuo gave an oil, which was purified by preparative TLC. The yields of pure products are given in Table 3.

Oxidative Deprotection of Allyl *n*-Decyl Ether (6a). To a stirred mixture of the peroxyiodane **1a** (202 mg, 0.60 mmol) and potassium carbonate (166 mg, 1.20 mmol) in cyclohexane (5 mL) was added the allyl ether **6a** (60 mg, 0.30 mmol) under an atmosphere at room temperature, and the mixture was stirred for 3 days. After evaporation of the solvent in vacuo and addition of a solution of NaOH (360 mg, 9.0 mmol) in methanol (6 mL) and water (1.5 mL), the mixture was stirred for 6 h at room temperature under nitrogen. The mixture was poured into an aqueous solution of $Na_2S_2O_3$ and extracted with dichloromethane, and the organic phase was washed with brine. The solution was dried over anhydrous Na_2SO_4 and concentrated. Flash chromatography (10% ethyl acetate in *n*-hexane) of the crude product yielded 1-decanol (35.4 mg, 74%).

Oxidative Deprotection of Allyl Menthyl Ether (6e). The allyl ether **6e** (20 mg, 0.10 mmol) was treated with the peroxyiodane **1a** (67 mg, 0.20 mmol) and cesium carbonate (130 mg, 0.40 mmol) in cyclohexane (5 mL) under an atmosphere at room temperature for 68 h. After evaporation of the solvent in vacuo, the mixture was further treated with a solution of KOH (168 mg, 3.0 mmol) in methanol (1.5 mL) and water (0.4 mL) at room temperature for 18 h under nitrogen. Flash chromatography (2% ethyl acetate in *n*-hexane) of the crude product yielded 1-menthol (10.7 mg, 68%).

Oxidative Deprotection of *n*-Decyl 3-Methyl-2-butenyl Ether (10a). The allyl ether **10a** (67 mg, 0.30 mmol) was treated with the peroxyiodane **1a** (202 mg, 0.60 mmol) and potassium carbonate (166 mg, 1.20 mmol) in cyclohexane (4 mL) under an atmosphere at room temperature for 3 days. After evaporation of the solvent in vacuo, the mixture was further treated with a solution of NaOH (360 mg, 9.0 mmol) in methanol (6 mL) and water (1.5 mL) at room temperature for 3 h under nitrogen. Flash chromatography (10% ethyl acetate in *n*-hexane) of the crude product yielded 1-decanol (37.4 mg, 80%).

Oxidation of *n*-Decyl Propargyl Ether (14a) with the Peroxyiodane 1a. To a stirred mixture of the peroxyiodane **1a** (135 mg, 0.40 mmol) and potassium carbonate (55 mg, 0.40 mmol) in cyclohexane (5 mL) was added the propargyl ether **14a** (45 mg, 0.20 mmol) under an atmosphere at room temperature, and the mixture was stirred for 62 h. The resulting precipitate, which contains potassium salt of *o*-iodobenzoic acid and potassium carbonate, was filtered off and washed with dichloromethane several times. Concentration in vacuo gave an oil, which was purified by preparative TLC (*n*-hexane−ethyl acetate−dichloromethane 95:5:0.5) to give the alkynyl ester **15a** (21.5 mg, 51%):[82] colorless oil; IR (film) 2927, 2121, 1718, 1467, 1234, 757 cm^{-1}; ^{1}H NMR δ 4.19 (t, $J = 6.6$ Hz, 2 H), 2.87 (s, 3 H), 1.89 (s, 1 H), 1.80−1.52 (m, 2 H), 1.48−1.16 (14 H), 0.88 (t, $J = 6.6$ Hz, 3 H); MS *m*/*z* (rel intensity) 195 (1), 97 (27), 83 (53), 69 (61), 57 (100).

Oxidation of *n*-Decyl 2-Pentynyl Ether (14b) with the Peroxyiodane 1a. The propargyl ether **14b** (34 mg, 0.15 mmol) was treated with the peroxyiodane **1a** (101 mg, 0.30 mmol) and potassium carbonate (83 mg, 0.60 mmol) in cyclohexane (5 mL) under an atmosphere at room temperature for 72 h. Preparative TLC (*n*-hexane−ethyl acetate−dichloromethane 95:5:0.5) gave the alkynyl ester **15b** (21.8 mg, 61%): colorless oil; IR (film) 2920, 2850, 2240, 1708, 1457, 1310, 1250, 1081, 1055, 757 cm^{-1}; ^{1}H NMR δ 4.15 (t, $J = 6.7$ Hz, 2 H), 2.35 (q, $J = 7.6$ Hz, 2 H), 1.76−1.52 (m, 2 H), 1.48−1.08 (m, 14 H), 1.21 (t, $J = 7.6$ Hz, 3 H), 0.88 (t, $J = 6.9$ Hz, 3 H); MS *m*/*z* (rel intensity) 238 (3, M^+), 140 (19), 111 (11), 99 (100), 81 (81), 69 (28), 57 (34), 43 (28); HRMS, calcd for $C_{15}H_{26}O_2$ (M^+) 238.1933, found 238.1906.

Oxidation of *n*-Decyl 3-(Trimethylsilyl)-2-propynyl Ether (14c) with the Peroxyiodane 1a. The propargyl ether **14c** (27 mg, 0.10 mmol) was treated with the peroxyiodane **1a** (67 mg, 0.20 mmol) and potassium carbonate (28 mg, 0.20 mmol) in cyclohexane (3 mL) under an atmosphere at room temperature for 60 h. Preparative TLC (*n*-hexane−ethyl acetate−dichloromethane 95:5:0.5) gave the alkynyl ester **15c** (21.9 mg, 65%): colorless oil; IR (film) 2910, 2850, 2170, 1710, 1460, 1345, 1250, 1220, 1100, 990, 845, 760 cm^{-1}; ^{1}H NMR δ 4.16 (t, $J = 6.5$ Hz, 2H), 1.84−1.50 (m, 2 H), 1.50−1.10 (m, 14 H), 0.88 (t, $J = 6.4$ Hz, 3 H), 0.25 (s, 9 H); MS *m*/*z* (rel intensity) 283 (4, $M^+ + 1$), 267 (25), 209 (26), 143 (100), 125 (49), 97 (27), 83 (33), 75 (36), 43 (26); HRMS, calcd for $C_{16}H_{30}O_2Si$ (M^+) 282.2015, found 282.1990.

Oxidation of 1-(Allyloxy)-5-(benzyloxy)-3-methylpentane (16a). The ether **16a** (23 mg, 0.10 mmol) was treated with the peroxyiodane **1a** (67 mg, 0.20 mmol) and cesium carbonate (65 mg, 0.20 mmol) in cyclohexane (5 mL) under an atmosphere at room temperature for 4 days. Preparative TLC (*n*-hexane−ethyl acetate−dichloromethane 90:10:0.5) gave 5-(benzyloxy)-3-methylpentyl acrylate (**16b**) (3.7 mg, 15%), 3-methyl-5-(2-propenyloxy)pentyl benzoate (**16c**) (4 mg, 16%), and 5-(benzoyloxy)-3-methylpentyl acrylate (**16d**) (8.5 mg, 33%). **16b**: colorless oil; IR (film) 2928, 1724, 1455, 1408, 1275, 1192, 1070, 812, 714 cm^{-1}; ^{1}H NMR δ 7.37−7.26 (m, 5 H), 6.39 (dd, $J = 17.3$, 1.7 Hz, 1 H), 6.11 (dd, $J = 17.3$, 10.3 Hz, 1 H), 5.80 (dd, $J = 10.3$, 1.7 Hz, 1 H), 4.50 (s, 2 H), 4.20 (t, $J = 7.1$ Hz, 2 H), 3.51 (t, $J = 6.7$ Hz, 2 H), 1.84−1.38 (m, 5 H), 0.94 (d, $J = 6.4$ Hz, 3 H); MS *m*/*z* (rel intensity) 262 (M^+), 190 (14), 162 (16), 107 (81), 91 (100), 83 (36), 77 (19), 55 (80); HRMS, calcd for $C_{16}H_{22}O_3$ (M^+) 262.1569, found 262.1561. **16c**: colorless oil; IR (film) 2928, 1722, 1454, 1275, 1111, 1028, 714 cm^{-1}; ^{1}H NMR δ 8.04 (br d, $J = 8.1$ Hz, 2 H), 7.56 (br t, $J = 8.1$, 1 H), 7.43 (br t, $J = 8.1$ Hz, 2 H), 5.90 (ddt, $J = 17.5$, 10.0, 5.6 Hz, 1 H), 5.26 (br d, $J = 17.5$ Hz, 1 H), 5.16 (br d, $J = 10.0$ Hz, 1 H), 4.37 (t, $J = 6.6$ Hz, 2 H), 3.96 (d, $J = 5.6$ Hz, 2 H), 3.50 (t, $J = 5.9$ Hz, 2 H), 1.96−1.35 (m, 5 H), 1.00 (d, $J = 5.9$ Hz, 3 H); MS *m*/*z* (rel intensity) 262 (M^+), 205 (3), 149 (13), 105 (87), 91 (100), 83 (29), 77 (31), 55 (31), 41 (29); HRMS, calcd for $C_{16}H_{22}O_3$ (M^+) 262.1569, found 262.1570. **16d**: colorless oil; IR (film) 2961, 1723, 1603, 1453, 1409, 1315, 1276, 1192, 1113, 1070, 1027, 985, 811, 713 cm^{-1}; ^{1}H NMR δ 8.03 (br d, $J = 7.8$ Hz, 2 H), 7.56 (br t, $J = 7.0$ Hz, 1 H), 7.43 (br t, $J = 7.8$ Hz, 2 H), 6.38 (dd, $J = 17.3$, 1.2 Hz, 1 H), 6.09 (dd, $J = 17.3$, 10.3 Hz, 1 H), 5.79 (dd, $J = 10.3$, 1.2 Hz, 1 H), 4.38 (t, $J = 6.3$ Hz, 2 H), 4.24 (t, $J = 5.8$ Hz, 2 H), 1.96−1.50 (m, 5 H), 1.03 (d, $J = 6.1$ Hz, 3 H); MS *m*/*z* (rel intensity) 277 ($M^+ + 1$), 204 (3), 123 (7), 105 (100), 82 (64), 77 (29), 67 (27), 55 (26); HRMS, calcd for $C_{16}H_{20}O_4$ (M^+) 276.1362, found 276.1368.

Oxidation of 5-(Benzyloxy)-3-methyl-1-(3-methyl-2-butenyloxy)pentane (17a). The ether **17a** (28 mg, 0.10 mmol) was treated with the peroxyiodane **1a** (135 mg, 0.40 mmol) and cesium carbonate (130 mg, 0.40 mmol) in cyclohexane (5 mL) under an atmosphere at room temperature for 74 h. Preparative TLC (*n*-hexane−ethyl acetate−dichloromethane 90:10:0.5) gave 5-(benzoyloxy)-3-methylpentyl 3-methyl-2-butenoate (**17b**) (15.5 mg, 52%): colorless oil; IR (film) 2950, 1715, 1650, 1600, 1450, 1380, 1315, 1275, 1230, 1150, 1110, 1075, 850, 715 cm^{-1}; ^{1}H NMR δ 8.03 (br d, $J = 7.1$ Hz, 2 H), 7.56 (br t, $J = 7.1$ Hz, 1 H), 7.43 (br t, $J = 7.1$ Hz, 2 H), 5.65 (br s, 1 H), 4.38 (t, $J = 6.5$ Hz, 2 H), 4.16 (dt, $J = 1.7$, 6.6 Hz, 2 H), 2.15 (d, $J = 1.0$ Hz, 3 H), 1.96−1.30 (m, 5 H), 1.87 (d, $J = 1.2$ Hz, 3 H), 1.02 (d, $J = 6.4$ Hz, 3 H); MS *m*/*z* (rel intensity) 304 (15, M^+), 105 (100), 83 (65), 77 (29), 55 (28); HRMS, calcd for $C_{18}H_{24}O_4$ (M^+) 304.1675, found 304.1682.

General Procedure for Oxidation of Arenes with the Peroxyiodane 1a. To a stirred mixture of the peroxyiodane **1a** (202 mg, 0.60 mmol) and cesium carbonate (391 mg, 1.20 mmol) in benzene (5 mL) was added an arene (0.20 mmol) under nitrogen at room temperature, and the mixture was stirred for the periods shown in Table 4. In some experiments, rubidium carbonate or potassium carbonate was used. The resulting precipitate was filtered off and washed with dichloromethane several times. Concentration in vacuo and preparative TLC gave pure products. The yields of pure products are given in Table 4. In some experiments, yields were determined by gas chromatography.

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(82) Baldwin, J. E.; Adlington, R. M.; Ramcharitar, S. H. *Tetrahedron* **1992**, *48*, 3413.

Oxidation of Fluorene (18a) without Base. Fluorene (**18a**) (33 mg, 0.20 mmol) was treated with the peroxyiodane **1a** (88 mg, 0.26 mmol) in dichloromethane (2 mL) at room temperature for 10 days under nitrogen. Preparative TLC gave 9-fluorenone (**19a**) (30 mg, 84%).

When the reaction was quenched after 24 h at room temperature, preparative TLC gave 9-fluorenone (**19a**) (3 mg, 9%) and 9-(*tert*-butylperoxy)fluorene (**20**) (8 mg, 15%), in addition to the recovered **18a** (20 mg, 60%). **20**: colorless prisms; mp 100−101 °C;[19] IR (film) 2981, 1451, 1363, 1195, 767, 743 cm^{-1}; ^{1}H NMR δ 7.73 (br d, J = 7.4, 2 H), 7.63 (br d, J = 7.4 Hz, 2 H), 7.38 (dt, J = 7.4, 1.2 Hz, 2 H), 7.28 (dt, J = 7.4, 1.2 Hz, 2 H), 5.95 (s, 1 H), 1.35 (s, 1 H); MS *m/z* (rel intensity) 254 (4, M^+), 181 (21), 165 (100), 152 (25), 83 (17); HRMS, calcd for $C_{17}H_{18}O_2$ (M^+) 254.1307, found 254.1298. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 79.79; H, 6.99.

Oxidation of 3β-Acetoxy-5-androsten-17-one (21a).[83] The olefin **21a** (33 mg, 0.10 mmol) was treated with the peroxyiodane **1a** (67 mg, 0.20 mmol) and potassium carbonate (55 mg, 0.40 mmol) in benzene (5 mL) under an atmosphere at room temperature for 80 h. Preparative TLC (40% ethyl acetate in *n*-hexane) gave 3β-acetoxy-5-androstene-7,17-dione (**22a**) (27.7 mg, 81%):[84] colorless prisms; mp 165−166 °C (recrystallized from dichloromethane−methanol); IR ($CHCl_3$) 2940, 2850, 1730, 1665, 1370, 1225 cm^{-1}; ^{1}H NMR δ 5.76 (s, 1 H), 4.85−4.67 (m, 1 H), 2.94−1.12 (m, 17 H), 2.06 (s, 3 H), 1.24 (s, 3 H), 0.90 (s, 3 H); MS *m/z* (rel intensity) 344 (4, M^+), 284 (100), 256 (21), 187 (15), 161 (21), 134 (15); HRMS, calcd for $C_{21}H_{28}O_4$ (M^+) 344.1988, found 344.1989.

Oxidation of Cholesteryl Acetate (21b). The olefin **21b** (86 mg, 0.20 mmol) was treated with the peroxyiodane **1a** (135 mg, 0.40 mmol) and potassium carbonate (111 mg, 0.80 mmol) in benzene (4 mL) under nitrogen at room temperature for 3 days. Preparative TLC (20% ethyl acetate in *n*-hexane) gave 3β-acetoxy-5-cholesten-7-one (**22b**) (54.5 mg, 62%):[85] colorless needles; mp 165−166 °C (recrystallized from dichloromethane−methanol); IR (KBr) 2948, 1734, 1673, 1633, 1242, 1038 cm^{-1}; ^{1}H NMR δ 5.71 (s, 1 H), 4.84−4.64 (m, 1 H), 2.70−0.90 (26 H), 2.05 (s, 3 H), 1.21 (s, 3 H), 0.92 (d, J = 6.4 Hz, 3 H), 0.87 (d, J = 6.6 Hz, 6 H), 0.68 (s, 3 H). Anal. Calcd for $C_{29}H_{46}O_3$: C, 78.68; H, 10.47. Found: C, 78.30; H, 10.75.

Oxidation of Benzyl Cholesteryl Ether (21c). According to the general procedure, the benzyl ether **21c** (95 mg, 0.20 mmol) was treated with **1a** (148 mg, 0.40 mmol) and potassium carbonate (111 mg, 0.80 mmol) at room temperature for 4 days. The crude product was purified by preparative TLC to give the keto ester **22c** (55 mg, 55%):[86] colorless needles; mp 161−162 °C (recrystallized from dichloromethane−methanol); IR (KBr) 2951, 1718, 1674, 1635, 1451, 1273, 1115, 713 cm^{-1}; ^{1}H NMR δ 8.04 (d, J = 8.0 Hz, 2 H), 7.57 (t, J = 8.0 Hz, 1 H), 7.44 (t, J = 8.0 Hz, 2 H), 5.75 (s, 1 H), 5.08−4.85 (m, 1 H), 2.80−0.90 (26 H), 1.26 (s, 3 H), 0.93 (d, J = 6.6 Hz, 3 H), 0.87 (d, J = 6.6 Hz, 6 H), 0.69 (s, 3 H); MS *m/z* (rel intensity) 504 (1, M^+), 382 (100), 269 (17), 174 (88), 161 (24), 119 (45), 105 (71) 51 (75); HRMS, calcd for $C_{34}H_{48}O_3$ (M^+) 504.3602, found 504.3602.

Oxidation of 2d in the Presence of Radical Inhibitor (Entries 5, 6, and 11−14 in Table 5). To a mixture of the peroxyiodane **1a**, a radical inhibitor, and potassium carbonate in benzene (5 mL) was added the benzyl ether **2d** (33 mg, 0.20 mmol) under nitrogen using a rubber balloon at 30 °C, and the mixture was stirred for the periods shown in Table 5. The yield of the benzoate **3d** and the recovered **2d** was determined by gas chromatography using *n*-tridecane as an internal standard and is shown in Table 5.

Reaction of Benzyl 3-Butenyl Ether (23) with the Peroxyiodane 1a. According to the general procedure, benzyl 3-butenyl ether (**23**) (33 mg, 0.20 mmol) was treated with **1a** (148 mg, 0.40 mmol) and potassium carbonate (111 mg, 0.80 mmol) at room temperature for 4 days. The crude product was purified by preparative TLC to give 3-butenyl benzoate (**24**) (20 mg, 58%) and the *tert*-butylperoxy acetal **25** (1.0 mg, 2%). **24**: colorless oil; IR (film) 2958, 1723, 1643, 1603, 1452, 1382, 1315, 1276, 1177, 1113, 1027, 919, 773, 7125 cm^{-1}; ^{1}H NMR δ 8.04 (br d, J = 7.7 Hz, 2 H), 7.60−7.26 (m, 3 H), 5.88 (ddt, J = 17.1, 10.3, 6.6 Hz, 1 H), 5.18 (br d, J = 17.1 Hz, 1 H), 5.11 (br d, J = 10.3 Hz, 1 H), 4.38 (t, J = 6.8 Hz, 2 H), 2.53 (tq, J = 1.5, 6.8 Hz, 2 H); MS *m/z* (rel intensity) 176 (M^+), 105 (100), 77 (43), 54 (51); HRMS, calcd for $C_{11}H_{12}O_2$ (M^+) 176.0837, found 176.0823. **25**: colorless oil; IR (film) 2979, 2928, 1642, 1455, 1364, 1197, 1100, 772, 698 cm^{-1}; ^{1}H NMR δ 7.48 (m, 2 H), 7.36 (m, 3 H), 5.87 (ddt, J = 17.1, 10.0, 6.6 Hz, 1 H), 5.85 (s, 1 H), 5.10 (m, 1 H), 5.03 (m, 1 H), 4.02 (dt, J = 9.7, 6.8 Hz, 1 H), 3.73 (dt, J = 9.7, 6.8 Hz, 1 H), 2.44 (tq, J = 1.2, 6.8 Hz, 2 H), 1.28 (s, 9 H); MS *m/z* (rel intensity) 161 (23), 131 (29), 105 (100), 91 (35), 77 (56), 55 (88); HRMS, calcd for $C_{11}H_{13}O_3$ ($M^+ - t$-Bu) 193.0864, found 193.0861.

Reaction of Benzyl 4,4-Diphenyl-3-butenyl Ether (26) with the Peroxyiodane 1a. According to the general procedure, 4,4-diphenyl-3-butenyl ether **26** (29 mg, 0.091 mmol) was treated with **1a** (61 mg, 0.18 mmol) and potassium carbonate (50 mg, 0.36 mmol) at room temperature for 6 days. The crude product was purified by preparative TLC to give the epoxy ester (**27**) (15 mg, 46%): colorless oil; IR (film) 1723, 1602, 1451, 1275, 1111, 764, 703 cm^{-1}; ^{1}H NMR δ 8.04 (dd, J = 7.1, 4.6 Hz, 2 H), 7.56 (t, J = 6.4 Hz, 1 H), 7.45−7.25 (m, 12 H), 4.47 (dd, J = 7.1, 6.1 Hz, 2 H), 3.63 (dd, J = 7.1, 4.7 Hz, 2 H), 2.01 (ddt, J = 14.9, 4.7, 7.1 Hz, 1 H), 1.70 (ddt, J = 14.9, 7.1, 6.1 Hz, 1 H); ^{13}C NMR δ 166.5, 140.6, 137.2, 133.0, 130.1, 129.6, 128.4, 128.3, 128.3, 128.0, 127.9, 127.8, 127.1, 66.2, 63.4, 62.1, 29.3; MS *m/z* (rel intensity) 344 (M^+), 239 (13), 222 (14), 194 (37), 165 (100), 149 (26), 105 (90), 83 (35), 77 (47), 57 (31); HRMS, calcd for $C_{23}H_{20}O_3$ (M^+) 344.1413, found 344.1396. The structure of **27** was unambiguously determined by two-dimensional (2D) NMR techniques, *i.e.*, ^{1}H,^{1}H-correlated spectroscopy (COSY) and ^{13}C,^{1}H-correlated spectroscopy via long-range coupling spectroscopy (COLOC).

Oxidation of Benzyl Ether 2d in the Presence of TEMPO. To a benzene (5 mL) solution of the peroxyiodane **1a** (135 mg, 0.40 mmol) in a glass ampule were added the benzyl ether **2d** (33 mg, 0.20 mmol), potassium carbonate (110 mg, 0.80 mmol), and 2,2,6,6-tetramethylpiperidine-*N*-oxyl (31 mg, 0.20 mmol). The reaction mixture was freeze−pump−thaw degassed (three cycles, 0.2 Torr) and flame sealed under argon. The mixture was stirred for 3 days at room temperature, and the resulting precipitate was filtered off and washed with dichloromethane several times. Concentration in vacuo gave an oil, which was purified by preparative TLC to give *n*-butyl benzoate (**3d**) (18.8 mg, 55%) and the TEMPO adduct **28** (18 mg, 28%). **28**: colorless oil; IR (film) 2900, 2850, 1430, 1355, 1340, 1110, 1060, 1000, 960, 940, 680 cm^{-1}; ^{1}H NMR δ 7.60−7.24 (m, 5 H), 5.72 (s, 1 H), 3.54−3.30 (m, 2 H), 1.80−0.90 (m, 10 H), 1.35 (s, 3 H), 1.17 (s, 3 H), 1.12 (s, 3 H), 1.00 (s, 3 H), 0.84 (t, J = 7.2 Hz, 3 H); FABMS *m/z* (rel intensity) 320 (3, $M^+ - 1$), 163 (100), 140 (72), 107 (100), 79 (8), 57 (10); HRFABMS, calcd for $C_{20}H_{33}NO_2$ (M^+) 319.2511, found 319.2466.

Oxidation of Isochroman (2v) in the Presence of TEMPO. To a benzene (5 mL) solution of the peroxyiodane **1a** (202 mg, 0.60 mmol) in a glass ampule were added isochroman (**2v**) (40 mg, 0.30 mmol), potassium carbonate (166 mg, 1.20 mmol), and TEMPO (47 mg, 0.30 mmol). The reaction mixture was degassed by freeze−pump−thaw (three cycles, 0.2 Torr) and sealed by flame under argon. The mixture was stirred for 2 days at room temperature, and the resulting precipitate was filtered off and washed with dichloromethane several times. Concentration in vacuo gave an oil, which was purified by preparative TLC to give 1-isochromanone (**3v**) (13 mg, 29%) and the TEMPO adduct **29** (38.2 mg, 44%). **29**: colorless plate; mp 89−91 °C (recrystallized from dichloromethane−methanol); IR ($CHCl_3$) 2930, 1600, 1453, 1365, 1315, 1130, 1090, 975, 955, 916 cm^{-1}; ^{1}H NMR δ 7.75−7.55 (m, 1 H), 7.38−7.00 (m, 3 H), 6.00 (s, 1 H), 4.02 (dt, J = 3.2, 10.7 Hz, 1 H), 3.87 (ddd, J = 10.7, 5.4, 3.2 Hz, 1 H), 2.93 (ddd, J = 16.1, 10.7, 5.4 Hz, 1 H), 2.67 (dt, J = 16.1, 3.2 Hz, 1 H), 1.78−0.87 (m, 6 H), 1.42 (s, 3 H), 1.30 (s, 6 H), 1.10 (s, 3 H); FABMS *m/z* (rel intensity) 290 (10, $M^+ + 1$), 140 (30), 133 (100); HRFABMS, calcd for $C_{18}H_{28}O_2N$ ($M^+ + 1$) 290.2120, found 290.2146.

Oxidation of *n*-Decyl Allyl Ether (6a) in the Presence of TEMPO. To a cyclohexane (5 mL) solution of the peroxyiodane **1a** (202 mg, 0.60 mmol) in a glass ampule were added *n*-decyl allyl ether (**6a**) (60 mg, 0.30 mmol), potassium carbonate (166 mg, 1.20 mmol), and TEMPO (47 mg, 0.30 mmol). The reaction mixture was degassed by freeze−pump−thaw (three cycles, 0.2 Torr) and sealed by flame under argon. The mixture was stirred for 3 days at room temperature, and

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the resulting precipitate was filtered off and washed with dichloromethane several times. Concentration in vacuo gave an oil, which was purified by preparative TLC to give *n*-decyl acrylate (**7a**) (8.1 mg, 13%) and the TEMPO adduct **30** (58.3 mg, 55%). **30**: colorless oil; IR (film) 2920, 2850, 1460, 1375, 1360, 1130, 1060, 970, 710 cm^{-1}; ^{1}H NMR δ 5.82 (ddd, J = 17.6, 10.5, 5.6 Hz, 1 H), 5.31 (br d, J = 17.6 Hz, 1 H), 5.24 (br d, J = 10.5 Hz, 1 H), 5.04 (d, J = 5.6 Hz, 1 H), 3.54 (dt, J = 9.3, 7.1 Hz, 1 H), 3.44 (dt, J = 9.3, 6.6 Hz, 1 H), 2.10−0.96 (m, 34 H), 0.88 (t, J = 6.8 Hz, 3 H); FABMS *m/z* (rel intensity) 354 (20, M$^+$ + 1), 197 (31), 140 (100), 85 (17), 55 (20); HRFABMS, calcd for $C_{22}H_{44}O_2N$ (M$^+$ + 1) 354.3372, found 354.3381.

General Procedure for the Competition Experiments. To a stirred mixture of the peroxyiodane **1a** (34 mg, 0.10 mmol) and potassium carbonate (28 mg, 0.20 mmol) in benzene (3 mL) was added a solution of benzyl *n*-butyl ether (**2d**) (411 mg, 2.5 mmol) and a substituted benzyl *n*-butyl ether (2.5 mmol) in benzene (2 mL) under argon. The reaction was allowed to proceed at 30 ± 0.2 °C for 12 h and, after addition of an appropriate internal standard, analyzed directly without workup for the two esters by GC. Each reaction mixture was analyzed four to six times and averaged. The reaction was repeated two times, and the results are reported in Table 6. Relative reactivity of 1-phenylhexane (**18b**) and di-*n*-butyl ether was determined in a similar manner.

Preparation of Benzyl-α,α-*d*$_2$ *n*-Butyl Ether (2d-*d*$_2$). To a stirred suspension of sodium hydride (500 mg, 12.5 mmol, 60% dispersion in oil), washed with hexane three times, in *N*,*N*-dimethylformamide (20 mL) was added benzyl-α,α-*d*$_2$ alcohol (550 mg, 5.0 mmol, 99.8% isotopic purity) dropwise at room temperature under nitrogen, and the mixture was stirred for 1 h. *n*-Butyl bromide (1.71 g, 12.5 mmol) was added and stirring was continued for 24 h. The mixture was poured over ice and extracted with diethyl ether, and the organic phase was washed with water and brine. The solution was dried over anhydrous Na_2SO_4 and concentrated. Flash chromatography of the crude product mixture yielded **2d**-*d*$_2$ (709 mg, 85%): colorless oil; IR (film) 3028, 2959, 2872, 2072, 1496, 1446, 1380, 1227, 1115, 1026, 717 cm^{-1}; ^{1}H NMR δ 7.33 (m, 5 H), 3.46 (t, J = 6.4 Hz, 2 H), 1.69−1.25 (m, 4 H), 0.91 (t, J = 7.2 Hz, 3 H); MS *m/z* (rel intensity) 166 (2, M$^+$), 94 (61), 93 (100); HRMS, calcd for $C_{11}H_{14}D_2O$ (M$^+$) 166.1326, found 166.1322.

Deuterium Kinetic Isotope Effect. A. Competition between Benzyl-α,α-*d*$_2$ *n*-Butyl Ether (2d-*d*$_2$) and *n*-Butyl *p*-Chlorobenzyl Ether (2r). To a stirred mixture of the peroxyiodane **1a** (17 mg, 0.05 mmol) and potassium carbonate (14 mg, 0.10 mmol) in benzene (2 mL) was added a solution of benzyl-α,α-*d*$_2$ ether **2d**-*d*$_2$ (208 mg, 1.25 mmol) and *p*-chlorobenzyl ether **2r** (248 mg, 1.25 mmol) in benzene (1 mL) under argon, and the mixture was stirred at 30 ± 0.2 °C for 12 h. After addition of *n*-tridecane as an internal standard, the ratio **3r/3d** measured by GC was 13.4. The ratio was compared with the relative rate $k_{\mathbf{2r}}/k_{\mathbf{2d}} = 0.96$ in Table 6. The deuterium kinetic isotope effect $k_H/k_D = 14.0$ was obtained.

B. Competition between Benzyl-α,α-*d*$_2$ *n*-Benzyl Ether (2d-*d*$_2$) and *n*-Butyl *m*-Chlorobenzyl Ether (2s). To a stirred mixture of the peroxyiodane **1a** (17 mg, 0.05 mmol) and potassium carbonate (14 mg, 0.10 mmol) in benzene (2 mL) was added a solution of benzyl-α,α-*d*$_2$ ether **2d**-*d*$_2$ (208 mg, 1.25 mmol) and *m*-chlorobenzyl ether **2s** (248 mg, 1.25 mmol) in benzene (1 mL) under argon, and the mixture was stirred at 30 ± 0.2 °C for 12 h. After addition of *n*-tridecane as an internal standard, the ratio **3s/3d** measured by GC was 10.2. The ratio was compared with the relative rate $k_{\mathbf{2s}}/k_{\mathbf{2d}} = 0.84$ in Table 6. The deuterium kinetic isotope effect $k_H/k_D = 12.2$ was obtained.

Synthesis of *n*-Butyl α-(*tert*-Butylperoxy)benzyl Ether (5) from Benzaldehyde.[40] To a mixture of benzaldehyde di-*n*-butyl acetal[87] (4.73 g, 20.0 mmol) and RuCl$_3$·*n*H$_2$O (157 mg, 0.60 mmol) in benzene (10 mL) was added a solution of *tert*-butyl hydroperoxide (7.5 mL of 80% solution in di-*tert*-butyl peroxide, 60 mmol) in benzene (20 mL) dropwise at room temperature over a period of 1 h under argon, and the mixture was stirred for an additional 6 h. The mixture was diluted with diethyl ether, and the organic layer was washed with water and brine, dried over Na_2SO_4, and filtered. Evaporation of the filtrate followed by column chromatography on silica gel (*n*-hexane−diethyl ether−dichloromethane 400:5:0.5) gave the peroxy acetal **5** (2.02 g, 40%) as a colorless oil.

Synthesis of *n*-Butyl α-(Hydroperoxy)benzyl Ether (32). To a mixture of benzaldehyde di-*n*-butyl acetate (473 mg, 2.0 mmol) and RuCl$_3$·*n*H$_2$O (15.7 mg, 0.06 mmol) in benzene (3 mL) was added a solution of hydrogen peroxide[88] (6.9 mL of a 0.87 M solution in diethyl ether, 6 mmol) in benzene (3 mL) dropwise at room temperature over a period of 0.5 h under argon, and the mixture was stirred for an additional 1.5 h. The mixture was diluted with diethyl ether, and the organic layer was washed with water and brine, dried over Na_2SO_4, and filtered. Evaporation of the filtrate followed by column chromatography on silica gel (3% ethyl acetate in *n*-hexane) gave the hydroperoxy acetal **32** (62 mg, 16%): colorless oil; IR (film) 3382, 2960, 2874, 1455, 1309, 1202, 1098, 839, 754, 699 cm^{-1}; ^{1}H NMR δ 8.49 (s, 1 H), 7.56−7.29 (m, 5 H), 5.80 (s, 1 H), 3.90 (dt, J = 9.5, 6.5 Hz, 1 H), 3.64 (dt, J = 9.5, 6.5 Hz, 1 H), 1.82−1.32 (m, 4 H), 0.94 (t, J = 7.3 Hz, 3 H); MS *m/z* (rel intensity) 163 (48, M$^+$ − OOH), 123 (47), 107 (100), 105 (96), 77 (64), 56 (33); HRMS, calcd for $C_{11}H_{15}O$ (M$^+$ − OOH) 163.1123, found 163.1126.

Reaction of the *tert*-Butylperoxy Acetal 5 and the Hydroperoxy Acetal 32. To a solution of the peroxy acetal **5** (50 mg, 0.2 mmol) or the hydroperoxy acetal **32** (39 mg, 0.2 mmol) in benzene (5 mL) was added an additive shown in Table 7 under nitrogen using a rubber balloon at 30 °C, and the mixture was stirred for 3 days. After cooling to 0 °C, the yields of the benzoate **3d** and the recovered acetal were determined by GC using *n*-tridecane and *n*-octane as internal standards, or by ^{1}H NMR analyses. The results are shown in Table 7.

Oxidation of Benzyl α-Methylbenzyl Ether (43). The ether **43** (318 mg, 1.5 mmol) was treated with the peroxyiodane **1a** (20 mg, 0.06 mmol) and potassium carbonate (17 mg, 0.12 mmol) in benzene (4 mL) under argon at 30 °C for 12 h. Analytical GC showed the formation of α-methylbenzyl benzoate (**44**) (20%), acetophenone (79%), and benzaldehyde (67%). These yields are based on the peroxyiodane **1a**. A pure sample of **44** and acetophenone was obtained by preparative TLC. **44**: colorless oil; IR (film) 2982, 1718, 1602, 1452, 1271, 1110, 1068, 712 cm^{-1}; ^{1}H NMR δ 8.09 (d, J = 7.1 Hz, 2 H), 7.6−7.2 (m, 8 H), 6.14 (q, J = 6.6 Hz, 1 H), 1.67 (d, J = 6.6 Hz, 3 H); MS *m/z* (rel intensity) 226 (8, M$^+$), 122 (16), 105 (100), 77 (67), 51 (42); HRMS, calcd for $C_{15}H_{14}O_2$ (M$^+$) 226.0993, found 226.0988. The authentic sample of **44** was prepared by the reaction of 1-phenylethanol with benzoyl chloride.

Rates of Decomposition of the Peroxyiodane 1a. Rates of decomposition of **1a** were measured by monitoring the decrease in absorbance at 275 nm at 30 ± 0.1 °C on a Shimadzu UV-160A spectrophotometer. A stock solution of **1a** was prepared by dissolving in acetonitrile (0.06 M). To 3.0 mL of dichloromethane in a quartz cuvette inserted in a cell compartment of the spectrophotometer and equilibrated at 30 °C was added 10 μL of the stock solution of **1a** from a microsyringe. The absorbance change was fed to a computer NEC PC-9801FA through an interface and processed by a pseudo-first-order kinetics program. The reaction followed pseudo-first-order kinetics for 4 half-lives, and the pseudo-first-order rate constant $k_{obsd} = 2.62 \times 10^{-5}$ s^{-1} was obtained.

Supporting Information Available: Spectroscopic data for compounds **3a**−**c**, **3e**−**z**, **7a**−**g**, **9**, **11a**−**c**, and **13** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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