Remarkable Substituent Effects on the Oxidizing Ability of Tetraarylbismuthonium Tetrafluoroborates in Alcohol Oxidation

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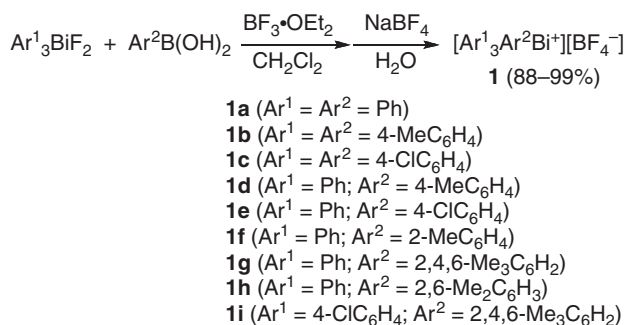
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Substituent effects on the oxidizing ability of tetraarylbismuthonium tetrafluoroborates in alcohol oxidation are reported. Intermolecular and intramolecular competition experiments on geraniol oxidation by the combined use of tetraarylbismuthonium tetrafluoroborates and N,N,N',N'-tetramethylguanidine (TMG) have revealed that the oxidizing ability of the bismuthonium salt increases by the introduction of methyl groups at the ortho position and an electron-withdrawing group at the para position of the aryl ligands. The intermolecular and intramolecular H/D kinetic isotope effects observed for the competitive oxidation of p-bromobenzyl alcohols have shown that the present oxidation reaction consists of fast pre-equilibrium leading to alkoxytetraarylbismuth(V) intermediates (first step) and α-hydrogen abstraction by the aryl ligand attached to the bismuth (second step). The experimental results demonstrate that the electron-deficient aryl ligands enhance the electrophilicity at the bismuth center to put forward the first step and that the bulky ligands destabilize the alkoxybismuth(V) intermediates to accelerate the second step. The newly explored mesityl- and 2,6-xylyltriarylbismuthonium salts have proven to convert primary and secondary alcohols to the corresponding carbonyl compounds with high efficiency under mild conditions. A remarkable steric effect of these oxidants has also been exhibited in the chemoselective oxidation between primary and secondary benzylic alcohols.

It is well known that organobismuth(V) compounds possess inherent oxidizing ability derived from the facile Bi^V/Bi^{III} redox process.[1] For instance, triarylbismuth(V) compounds of the type Ar_3BiX_2 (X = anionic ligands) convert a variety of primary and secondary alcohols to aldehydes and ketones, respectively, under mild conditions.[2] In the 80s, Barton and co-workers extensively studied alcohol oxidation using triarylbismuth(V) compounds from synthetic and mechanistic points of view, and disclosed that the oxidation of simple alcohols proceeds through two main steps; formation of alkoxytriarylbismuth(V) intermediates (first step) and α-hydrogen abstraction by an aryl ligand attached to the bismuth center (second step).[3] In the second step, carbonyl compounds are formed together with equimolar amounts of arene and diarylbismuth(III) species. This mechanism implies that the oxidizing ability of triarylbismuth(V) compounds strongly depends on the intrinsic character of the Bi-bound aryl ligands. In fact, Barton and co-workers reported some results of competition experiments on the oxidation of allylic alcohols by the Ar_3BiX_2/K_2CO_3 (X = Cl, Br, and ONO_2) system, in which the relative reactivity of Ar_3BiX_2 was estimated to be in the order Ar = 4-methylphenyl < phenyl < 4-chlorophenyl < 3-nitrophenyl.[4] Recently, we reported the first systematic study of the substituent effects on the oxidizing ability of triarylbismuth dichlorides (Ar_3BiCl_2) in alcohol oxidation, where the relative reactivity was determined quantitatively by intermolecular and intramolecular competitive experiments.[5] It has been disclosed that

aryl ligands bearing a methyl group at the ortho position and/or an electron-withdrawing group at the para position dramatically enhance the overall rate of oxidation in the Ar_3BiCl_2/base system. Hence, to design efficient organobismuth(V) oxidants, both the steric and electronic nature of the aryl ligands must be taken into consideration.

In contrast to triarylbismuth(V) compounds, only limited information is available for the oxidizing ability of other polyarylbismuth(V) compounds. In 1987, Barton and co-workers reported that tetraphenylbismuth tosylate and trifluoroacetate (Ph_4BiX; X = OTs and $OCOCF_3$) oxidized 3β-cholestanol and neopentyl alcohol under basic conditions.[6] Their pioneering work, however, has received little attention, and there has been no systematic study of the substituent effects on the oxidizing ability of tetraarylbismuth(V) compounds. Quite recently, we reported a new organobismuth(V) oxidant, mesityltriphenylbismuthonium tetrafluoroborate (mesityl = 2,4,6-trimethylphenyl), which efficiently converted a variety of primary and secondary alcohols to the corresponding carbonyl compounds in the presence of N,N,N',N'-tetramethylguanidine (TMG) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[7] Most importantly, the mesitylbismuthonium salt was found to oxidize the alcohols much more rapidly than the 4-methylphenyl- and phenyl-substituted bismuthonium salts. Such a remarkable rate enhancement can be explained by considering steric effects of the aryl ligands attached to the bismuth center; the bulky mesityl ligand is likely to accelerate the α-hydrogen ab-

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Oxidation with Bismuthonium Salts

$$\text{Ar}^1_3\text{BiF}_2 + \text{Ar}^2\text{B(OH)}_2 \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{BF}_3\cdot\text{OEt}_2} \xrightarrow[\text{H}_2\text{O}]{\text{NaBF}_4} [\text{Ar}^1_3\text{Ar}^2\text{Bi}^+][\text{BF}_4^-]$$

1 (88–99%)

1a (Ar¹ = Ar² = Ph)
1b (Ar¹ = Ar² = 4-MeC₆H₄)
1c (Ar¹ = Ar² = 4-ClC₆H₄)
1d (Ar¹ = Ph; Ar² = 4-MeC₆H₄)
1e (Ar¹ = Ph; Ar² = 4-ClC₆H₄)
1f (Ar¹ = Ph; Ar² = 2-MeC₆H₄)
1g (Ar¹ = Ph; Ar² = 2,4,6-Me₃C₆H₂)
1h (Ar¹ = Ph; Ar² = 2,6-Me₂C₆H₃)
1i (Ar¹ = 4-ClC₆H₄; Ar² = 2,4,6-Me₃C₆H₂)

Scheme 1. Synthesis of tetraarylbismuthonium tetrafluoro-borates **1a–1i**.

straction from sterically crowded alkoxybismuth(V) intermediates. These results suggested that more efficient tetraarylbismuth(V) oxidants could be explored by suitably tuning the steric and electronic characters of the aryl ligands. Thus, we set out to systematically investigate the substituent effects on the intrinsic oxidizing ability of tetraarylbismuthonium salts.

Here we report the first systematic study of intermolecular and intramolecular competition experiments on alcohol oxidation by using a series of tetraarylbismuthonium tetrafluoroborates. It has been revealed that both steric and electronic effects of the aryl substituents definitely affect the overall rate of the reaction. Oxidation of several alcohols and chemoselective oxidation between primary and secondary alcohols with newly developed tetraarylbismuth(V) oxidants are also reported.

Results and Discussion

To investigate the relative oxidizing abilities of tetraarylbismuthonium salts, we prepared a series of tetraarylbismuthonium tetrafluoroborates **1a–1i** according to a reported procedure:[8] reaction of triarylbismuth difluorides with arylboronic acids in the presence of BF₃·OEt₂, followed by treatment with an aqueous solution of NaBF₄ afforded **1a–1i** in high yield (Scheme 1). The bismuthonium salts **1a–1i** were purified by recrystallization from CH₂Cl₂–Et₂O and characterized by spectroscopic methods. In the MS spectra of **1a–1i**, intense peaks assignable to [Ar¹₃Ar²Bi]⁺ ions were detected, while in the IR spectra, strong absorptions due to BF₄⁻ ion were observed at 1150–950 cm⁻¹. These data indicate that each bismuth center in **1a–1i** essentially possesses onium nature. The structure of **1g** was further elucidated by X-ray crystallography. As shown in Figure 1, the bismuth center adopts a distorted tetrahedral geometry with C–Bi–C bond angles of 97.35(14)–125.26(14)° and Bi–C bond distances of 2.207(4)–2.212(4) Å. The Bi–F(1) distance [3.005(2) Å] is much longer than the sum of their covalent radii (2.17 Å), implying that the cationic bismuth center weakly interacts with the fluoroborate ion.

Scheme 2 depicts a plausible mechanism of the alcohol oxidation by tetraarylbismuthonium salt **1**. On the basis of the fact that equimolar amounts of arene and triarylbismuthane are produced together with carbonyl compound, the reaction is considered to proceed through two main steps; formation of alkoxytetraarylbismuth(V) intermediate **A** (first step) and production of carbonyl compound via α-hydrogen abstraction (second step). The first step is promoted by the addition
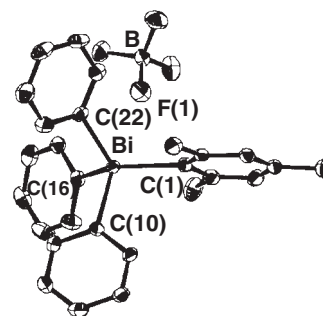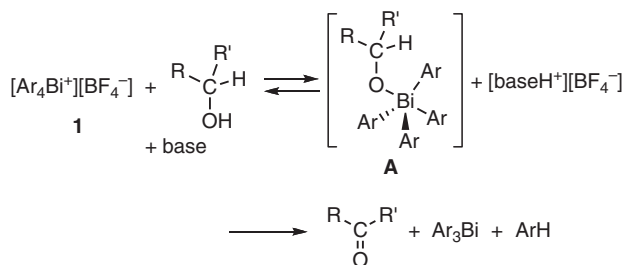

Figure 1. ORTEP diagram of **1g**. Selected bond lengths (Å) and angles (deg): Bi–C(1), 2.207(4); Bi–C(10), 2.208(4); Bi–C(16), 2.202(4); Bi–C(22), 2.212(4); Bi–F(1), 3.005(2); C(1)–Bi–C(10), 102.13(13); C(1)–Bi–C(16), 125.26(14); C(1)–Bi–C(22), 112.88(14); C(10)–Bi–C(16), 97.35(14); C(10)–Bi–C(22), 107.33(14); C(16)–Bi–C(22), 108.94(14).

**Scheme 2.** Plausible mechanism for alcohol oxidation.

Table 1. Oxidation of Benzyl Alcohol with **1g** in CDCl₃[a]

Entry	Base	Time/h	Yield[b]/%
1	TMG	1.5	>99
2	DBU	1.5	>99
3	Et₃N	20	31
4	K₂CO₃	1.5	66
5	Pyridine	4	0

a) Benzyl alcohol (0.050 mmol), **1g** (0.055 mmol), base (0.055 mmol), CDCl₃ (1 mL). b) Determined by ¹H NMR using DMF as an internal standard.

of a base. As shown in Table 1, TMG and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were found to promote the oxidation of benzyl alcohol with mesityltriphenylbismuthonium salt **1g** efficiently, whereas Et₃N and K₂CO₃ were less effective. No oxidation took place with pyridine even after 4 h in CDCl₃ at room temperature. Therefore, TMG was used as the base in the present competition experiments.

First, we determined the relative oxidizing ability of tetraarylbismuthonium salts by means of intermolecular competitive oxidation reactions using tetraphenylbismuthonium salt **1a** and ortho/para-substituted derivatives **1b**, **1c**, and **1f–1i** (Scheme 3 and Tables 2 and 3). TMG (1.1 equiv) was added to a CH₂Cl₂ solution containing geraniol **2** (5 × 10⁻³ M) (1 M = 1 mol dm⁻³) and two kinds of bismuthonium salts **1x**

Scheme 3. Competitive intermolecular oxidation of geraniol.
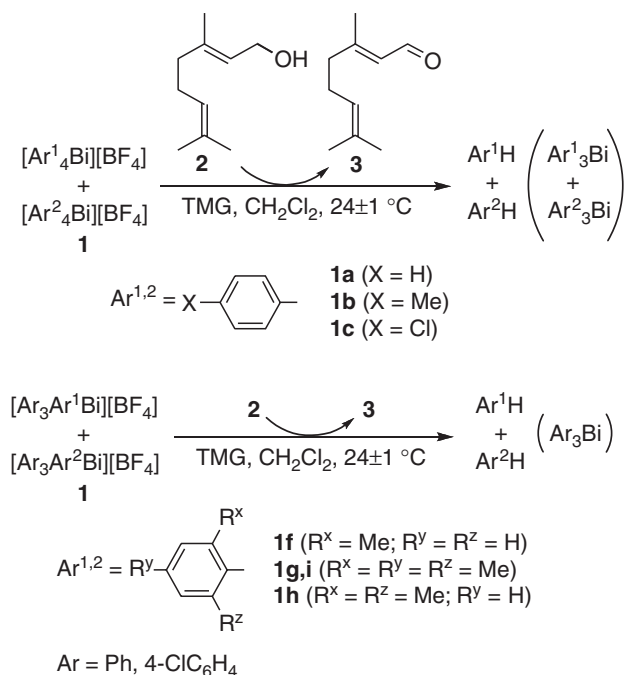
Table 2. Competitive Intermolecular Oxidation of **2** with **1**

| Entry	**1x**	Ar^1	**1y**	Ar^2	Ar^1H/Ar^2H[a]
1	**1a**	C_6H_5	**1b**	$4\text{-}MeC_6H_4$	89/11
2	**1a**	C_6H_5	**1c**	$4\text{-}ClC_6H_4$	2/98
3	**1a**	C_6H_5	**1g**	$2,4,6\text{-}Me_3C_6H_2$	4/96
4	**1c**	$4\text{-}ClC_6H_4$	**1i**	$2,4,6\text{-}Me_3C_6H_2$	32/68
5	**1f**	$2\text{-}MeC_6H_4$	**1g**	$2,4,6\text{-}Me_3C_6H_2$	9/91
6	**1g**	$2,4,6\text{-}Me_3C_6H_2$	**1h**	$2,6\text{-}Me_2C_6H_3$	33/67

a) Determined by GC.

and **1y** (each 3 equiv) at $24 \pm 1\,°C$. After **2** had been complete-ly oxidized to geranial (**3**), the reaction mixture was analyzed by gas chromatography (GC) and ^1H NMR spectroscopy. Table 2 summarizes the relative ratios of two kinds of arenes produced (Ar^1H/Ar^2H), which are indices of the relative over-all reaction rates. The quantitative formation of the corre-sponding triarylbismuthanes was confirmed by ^1H NMR spec-troscopy.[9] It should be noted that, in the oxidation using **1g–1i**, the mesityl and 2,6-xylyl ligands are cleaved with $\geq 99\%$ se-lectivity (vide infra). In Entry 4, the amount of chlorobenzene produced from **1i** is negligible as compared to that produced from **1c**, and, in Entries 5 and 6, only a trace amount ($<1\%$) of benzene could be detected. Therefore, the Ar^1H/Ar^2H ratios listed in Table 2 basically reflect the relative oxidizing ability of the bismuthonium salts examined.

On the basis of the Ar^1H/Ar^2H ratios observed for the com-petitive reactions using **1a–1c**, the electronic effects of para-substituted aryl ligands relative to phenyl were determined as follows: $4\text{-}MeC_6H_4$ (0.12) $< C_6H_5$ (1.0) $< 4\text{-}ClC_6H_4$ (49). Apparently, the overall reaction rate increases with in-creasing electron-withdrawing ability of the para substituents. Similarly, on the basis of the Ar^1H/Ar^2H ratios observed for the competitive reactions using **1a** and **1f–1h** the steric effects of ortho-substituted aryl ligands relative to phenyl were deter-

Table 3. Substituent Effects Obtained from the Competi-tion Experiments

Aryl ligand	Inter[a]	Intra[b]
$4\text{-}MeC_6H_4$	0.12	0.57
C_6H_5	1	1
$4\text{-}ClC_6H_4$	49	1.4
$2\text{-}MeC_6H_4$	2.4	22
$2,6\text{-}Me_2C_6H_3$	48	3.3×10^2
$2,4,6\text{-}Me_3C_6H_2$	24	3.7×10^2

a) Relative reactivity of **1b**, **1c**, and **1f–1h** vs. **1a**, obtained from the results shown in Table 2. b) Relative hydrogen-ab-stracting aptitude of aryl group vs. phenyl group, obtained from the results shown in Table 4.
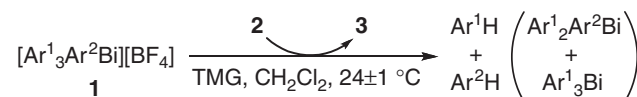
Scheme 4. Competitive intramolecular oxidation of geraniol.

Table 4. Competitive Intramolecular Oxidation of **2** with **1**

Entry	**1**	Ar^1	Ar^2	Ar^1H/Ar^2H[a]
1	**1d**	C_6H_5	$4\text{-}MeC_6H_4$	84/16
2	**1e**	C_6H_5	$4\text{-}ClC_6H_4$	68/32
3	**1f**	C_6H_5	$2\text{-}MeC_6H_4$	12/88
4	**1g**	C_6H_5	$2,4,6\text{-}Me_3C_6H_2$	0.8/99.2
5	**1h**	C_6H_5	$2,6\text{-}Me_2C_6H_3$	0.9/99.1
6	**1i**	$4\text{-}ClC_6H_4$	$2,4,6\text{-}Me_3C_6H_2$	1.4/98.6

a) Determined by GC.

mined as follows: Ph (1.0) $<$ $2\text{-}MeC_6H_4$ (2.1) $<$ $2,4,6\text{-}Me_3C_6H_2$ (24) $<$ $2,6\text{-}Me_2C_6H_3$ (48).[10] This result exhibits that the overall reaction rate is enhanced considerably by intro-ducing two methyl groups at the ortho (2,6-) positions. The fact that **1h** oxidizes **2** more rapidly than does **1g** is also attrib-utable to the difference in the electronic effect between mesityl and 2,6-xylyl ligands. In addition, the oxidizing ability of **1i** was found to be higher than that of **1c**, suggesting that the ster-ic effect induced by one mesityl ligand is slightly larger than the electronic effect induced by one chlorophenyl ligand.

To evaluate the substituent effects on the second step, we next examined intramolecular competitive oxidation reactions using tetraarylbismuthonium salts bearing two kinds of aryl groups ($[Ar^1_3Ar^2Bi^+][BF_4^-]$: **1d–1i**). This provides relative rate constants at which the Bi–C bond is cleaved via α-hydro-gen abstraction. Treatment of **1d–1i** with **2** in the presence of TMG in CH_2Cl_2 at $24 \pm 1\,°C$ gave two kinds of arenes and tri-arylbismuthanes (Scheme 4 and Table 4). On the basis of the relative ratios of the arenes (Ar^1H/Ar^2H) and the number of the aryl ligands originally attached to bismuth, the relative hydrogen-abstracting aptitudes were determined as follows: $4\text{-}MeC_6H_4$ (0.57) $<$ C_6H_5 (1.0) $<$ $4\text{-}ClC_6H_4$ (1.4) $<$ $2\text{-}MeC_6H_4$ (22) $<$ $2,6\text{-}Me_2C_6H_3$ (3.3×10^2) $<$ $2,4,6\text{-}Me_3C_6H_2$ (3.7×10^2).[11] Obviously, the electronic effect of the para sub-stituents is small as compared to that observed for the intermo-lecular competition experiments, suggesting that the α-hydro-gen is abstracted via a weakly polar transition state. In sharp contrast, the steric effect on the second step is significant, as

was observed for the alcohol oxidation by Ar_3BiCl_2. For instance, both mesityl and 2,6-xylyl ligands abstract the α-hydrogen >300 times faster than the phenyl ligand. The substituent effects on the reaction rates will be discussed later.

To get some insight into the rate-determining step of the present oxidation system, we also measured intermolecular and intramolecular H/D kinetic isotope effects for the α-hydrogen abstraction. The intermolecular competition reaction of **1g** with a mixture of p-BrC$_6$H$_4$CH$_2$OH and p-BrC$_6$H$_4$CD$_2$OH (each 3 equiv) afforded the corresponding p-bromobenzaldehydes (eq 1). Similarly, the intramolecular competitive reaction of **1g** with p-BrC$_6$H$_4$CH(D)OH was conducted (eq 2). In these reactions, mesitylenes (MesH/MesD) and triphenylbismuthane were formed in >99% yields. The kinetic isotope effects were determined by ^{1}H NMR spectroscopy based on the relative ratio of p-BrC$_6$H$_4$CHO/p-BrC$_6$H$_4$CDO. As listed in eqs 1 and 2, the observed intermolecular kinetic isotope effect ($k_{H/D} = 3.9 \pm 0.6$) is almost identical to the intramolecular kinetic isotope effect ($k'_{H/D} = 3.9 \pm 0.5$), indicating that the alcohol oxidation using **1** consists of fast pre-equilibrium (first step) and irreversible α-hydrogen abstraction (second step).[12] Therefore, it can be concluded that the rate-determining step involves the α-hydrogen abstraction by the aryl ligand.

$$\begin{array}{c} RCH_2OH + RCD_2OH \xrightarrow[\text{CDCl}_3,\ 24\pm1\ °C]{\mathbf{1g} + TMG} RCHO + RCDO \\ (R = p\text{-BrC}_6\text{H}_4) \qquad\qquad (-ArH)\ \ (-ArD) \\ k_{H/D} = 3.9\pm0.6 \end{array} \quad (1)$$

$$\begin{array}{c} RCH(D)OH \xrightarrow[\text{CDCl}_3,\ 24\pm1\ °C]{\mathbf{1g} + TMG} RCDO + RCHO \\ (R = p\text{-BrC}_6\text{H}_4) \qquad\qquad (-ArH)\ \ (-ArD) \\ k_{H/D} = 3.9\pm0.5 \end{array} \quad (2)$$
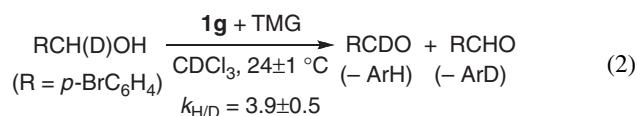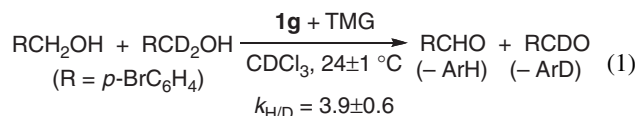
It is well known that the primary kinetic isotope effect on the concerted hydrogen abstraction reaction is related to the linearity of the X···H–C bond at the transition state (X = hydrogen-abstracting atom).[13] The four-fold preference for loss of H relative to D observed in the present intramolecular competition experiments suggests that the α-hydrogen is abstracted via a weakly polarized, cyclic transition state.[14] Thus, the hydrogen-abstracting aptitude of the aryl ligands should depend on bond dissociation energies of the Bi–C bonds of alkoxybismuth(V) intermediate **A**. Presumably, the Bi–C bonds of the mesityl and 2,6-xylyl ligands in **A** are weakened because of steric congestion around the bismuth center (vide supra).[15,16]

The substituent effects of the aryl ligands observed in the present study are summarized as follows. (1) The electronic effect observed for the overall step is appreciably larger than that observed for the second step. In other words, the first step is sensitive to the electronic character of the aryl ligands. With increasing electron-withdrawing ability of the para substituents, the electrophilicity of the bismuth center increases to accelerate the forward rate of the first step (Bi–O bond formation), and as a result, the pre-equilibrium is put forward to the right side. (2) The steric effect observed for the overall steps is considerably smaller than that observed for the second step. It is likely that the bulky aryl ligands, such as mesityl and 2,6-xylyl, kinetically protect the bismuth center to decelerate

the forward rate of the first step. (3) The second step is susceptible to the steric nature of the substituents. The introduction of methyl groups at the ortho positions destabilizes the alkoxy-tetraarylbismuth(V) intermediate **A** due to the steric congestion around the bismuth center.[17] As a consequence, the rate of α-hydrogen abstraction is accelerated significantly by the introduction of the mesityl and 2,6-xylyl ligand. Hence, to construct highly efficient onium-type Bi^V oxidants, it is desirable to introduce an electron-withdrawing substituent at the para position and/or moderately bulky substituents at the ortho positions by considering a balance between these two effects. In this context, triphenyl(2,6-xylyl)bismuthonium salt **1h** and tris(p-chlorophenyl)(mesityl)bismuthonium salt **1i** are promising oxidants similar to mesityltriphenylbismuthonium salt **1g**.

With new efficient organobismuth(V) oxidants **1g–1i** in hand, we examined the oxidation of some alcohols. As summarized in Table 5, primary and secondary alcohols were oxidized by **1g–1i**/TMG to aldehydes and ketones, respectively, at room temperature. The carbonyl compounds were easily separated from the bismuthane and the guanidinium salt by silica gel column chromatography. In the reaction of primary alcohols, overoxidation to carboxylic acids did not occur at all (Entries 1, 2, and 6). As expected, **1h** and **1i** oxidized the alcohols more rapidly than **1g**. In particular, the remarkable rate acceleration was observed for the reaction of secondary benzylic alcohols (Entries 3 and 4) and saturated alcohols (Entries 6 and 7) without noticeable side reactions. It is also noteworthy that **1g–1i** converted 2,2,2-trifluoro-1-phenylethanol to 2,2,2-trifluoro-1-phenylethanone within 0.5–1.5 h at room temperature (Entry 5).[18] The efficiency of this oxidation is appreciably higher than that of the Dess–Martin oxidation, which was reported to require excess oxidant (3.7 equiv) to obtain a good yield of the ketone.[18a] The above results clearly demonstrate the synthetic utility of tetraarylbismuthonium salts **1g–1i** as stoichiometric oxidants.[19]

Finally, we examined the competitive oxidation reactions between primary (1°) and secondary (2°) alcohols using tetraarylbismuthonium salts **1d** and **1f–1i**, tris(2-methylphenyl)-bismuth dichloride, and Dess–Martin periodinane (DMP) (Table 6). When a mixture of benzyl alcohol (PhCH$_2$OH) and benzylic secondary alcohol (PhCH(R)OH; R = Me, Et, and i-Pr) was treated with **1g**/TMG in CDCl$_3$ at 24 ± 1 °C, benzaldehyde (PhCHO) was produced predominantly over phenyl alkyl ketone (PhCOR; R = Me, Et, and i-Pr). In this series, the 1°/2° (PhCHO/PhCOR) selectivity increases from 81/19 to 94/6 with increasing the size of α-substituents (R) of the secondary benzylic alcohols. It should be emphasized that all of these alcohols are oxidized quantitatively by **1g**/TMG under the appropriate conditions. In the competitive reactions between benzyl alcohol and 1-phenyl-1-propanol (Entries 2 and 4–7), the mesityl and 2,6-xylyl-substituted derivatives **1g–1i** exhibit higher 1°/2° selectivities (91/9–92/8) than do the 4-methylphenyl and 2-methylphenyl derivatives **1d** and **1f** (74/26 and 77/23). These results imply that the first step is sensitive to bulkiness of the substrates as well as steric environment around the cationic bismuth center. Thus, not only the *ortho*-methyl groups of the oxidants but also the α-substituents of the alcohols retard the Bi–O bond-forming reaction (nucleophilic attack of the alcohol to the bismuth center) kinet-

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Table 5. Oxidation of Alcohols with **1g–1i**

$$ R \underset{OH}{\overset{R'}{\diagdown}} \xrightarrow[\text{solvent, r.t.}]{\substack{\textbf{1g-i} \text{ (1.1 equiv)} \\ \text{TMG (1.1 equiv)}}} R \underset{O}{\overset{R'}{\diagdown}} $$

Entry	Alcohol	Solvent	Time/h, Yield/%		
			1g	**1h**	**1i**
1	O_2N–C$_6$H$_4$–CH$_2$OH	CH_2Cl_2	1.0, 99[a]	0.5, 95[a]	0.5, 92[a]
2	(geranyl-type alcohol) OH	CH_2Cl_2	0.5, 98[a]	0.5, 99[a]	0.5, 99[a]
3	Ph–C(Me)(H)OH	CH_2Cl_2	4.0, 91[a]	0.5, 96[a]	0.5, 88[a]
4	Ph–C(Et)(H)OH	$CDCl_3$	40, 88[b]	1.0, 87[b]	1.0, 99[b]
5	Ph–C(CF$_3$)(H)OH	$CDCl_3$	1.5, 94[b]	1.0, 99[b]	0.5, 99[b]
6	$CH_3CH_2CH_2CH_2CH_2OH$	Toluene-d_8	1.5, 99[b]	0.5, 88[b]	0.5, 97[b]
7	Et–C(Et)(H)OH	Toluene-d_8	3.0, 98[b]	1.5, 88[b]	0.5, 97[b]

a) Isolated yield. b) NMR yield.

Table 6. Chemoselective Oxidation of Primary/Secondary Alcohols

$$ \underset{OH}{\overset{H}{Ph\diagdown}} + \underset{OH}{\overset{R}{Ph\diagdown}} \xrightarrow[\text{CDCl}_3,\ 24\pm1\ ^\circ\text{C}]{\substack{\textbf{oxidant} \text{ (0.9 equiv)} \\ \text{TMG (1.0 equiv)}}} \underset{O}{\overset{H}{Ph\diagdown}} + \underset{O}{\overset{R}{Ph\diagdown}} $$

Entry	Oxidant	R	Time/h	PhCHO/PhCOR[a]
1	**1g**	Me	1	81/19
2	**1g**	Et	1	92/8
3	**1g**	*i*-Pr	1	94/6
4	**1d**	Et	7	74/26
5	**1f**	Et	7	77/23
6	**1h**	Et	0.5	92/8
7	**1i**	Et	0.5	91/9
8	$(2\text{-MeC}_6\text{H}_4)_3\text{BiCl}_2$	Et	3	63/37
9	DMP[b]	Et	2	67/33

a) Determined by ^{1}H NMR. b) TMG was not added.

ically. Note that the 1°/2° selectivities attained by tetraarylbismuthonium salts **1g–1i** are considerably higher than those observed for tris(2-methylphenyl)bismuth dichloride (63/37) and DMP (67/33) (Entries 8 and 9). Thus, **1g–1i** discriminate between steric bulkiness of the α-substituents (H vs. Et) of the alcohols more efficiently than other oxidants examined (Scheme 5). Although there exist more primary-selective oxidants,[20] tetraarylbismuthonium salts bearing bulky aryl ligands constitute a useful addition to the existing efficient oxidants.

Conclusion

In summary, we have elucidated the substituent effects on the oxidizing ability of tetraarylbismuthonium salts in alcohol oxidation by means of intermolecular and intramolecular competition experiments. It is now clear that highly efficient Bi^V oxidants of the type $[Ar^1_3Ar^2Bi^+][BF_4^-]$ can be constructed by the introduction of bulky aryl ligands and/or electron-deficient aryl ligands. The bulky aryl ligands seem to weaken the Bi–C bond and dramatically accelerate the α-hydrogen abstraction step, whereas the electron-deficient aryl ligands enhance the electrophilicity of the bismuth center and put forward the pre-equilibrium leading to alkoxybismuth(V) intermediates. The newly explored mesityl- and 2,6-xylyl-triarylbismuthonium tetrafluoroborates have proven to convert primary and secondary alcohols to the corresponding carbonyl compounds in the presence of TMG with high efficiency under mild conditions. A remarkable steric effect of these oxidants has also been exhibited in the chemoselective oxidation between primary and secondary benzylic alcohols.

Experimental

General.   All melting points were determined on a Yanagimoto hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a JEOL EX-400 (400 MHz) or a JEOL AL300 (300 MHz) spectrometer using CDCl$_3$ as the solvent unless otherwise noted. Chemical shifts are reported as relative values vs. tetramethylsilane. IR spectra were observed as KBr pellets on a Shimadzu FTIR-8200A spectrophotometer. MALDI-TOF mass spectra were measured on a Shimadzu MALDI-I spectrometer using CHCA as a matrix. GC was performed on a Shimadzu GC-14A fitted with a silica gel capillary column. Elemental analyses were performed at the Microanalytical Laboratory of Kyoto University. Dichloromethane and toluene were distilled from calcium hydride before use. Crystallographic data of **1g** was reported previously[7] and has been deposited with Cambridge Crystallo-
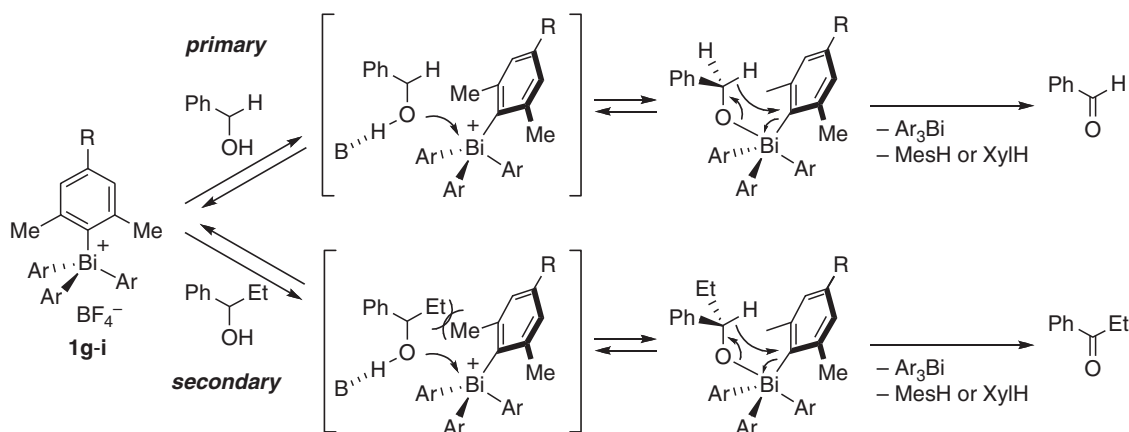
Scheme 5. Chemoselective oxidation of benzyl alcohol and 1-phenyl-1-propanol by **1g–1i**.

graphic Data Centre: Deposition number CCDC-635005. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Compounds. Tetraarylbismuthonium salts **1a–1i** were prepared from triarylbismuth difluorides, BF$_3$·OEt$_2$, and arylboronic acids as described below.[8] *p*-Bromobenzyl alcohol-α-*d*[21] and *p*-bromobenzyl alcohol-α,α-*d*$_2$[22] were prepared by reduction of *p*-bromobenzaldehyde and *p*-bromobenzoic acid ethyl ester, respectively, with LiAlD$_4$. TMG was purified by distillation. Other reagents were used as commercially received.

Tetraarylbismuthonium Tetrafluoroborates 1.   Typical Procedure: BF$_3$·OEt$_2$ (0.78 mL, 6.0 mmol) was added to a CH$_2$Cl$_2$ solution (25 mL) containing triphenylbismuth difluoride (2.39 g, 5.00 mmol) and mesitylboronic acid (0.90 g, 5.5 mmol) at 0 °C, and the mixture was stirred for 2 h at room temperature. An aqueous solution of NaBF$_4$ (17 g, 150 mmol) was then added, and the resulting two-phase solution was vigorously stirred for 20 min. The aqueous phase was separated and extracted with CH$_2$Cl$_2$. The combined organic extracts were dried over MgSO$_4$, passed through a short silica gel column, and evaporated under reduced pressure to leave a solid residue, which was reprecipitated from CH$_2$Cl$_2$–Et$_2$O to afford **1g** (3.17 g, 98%) as a colorless solid. ^{1}H NMR (CDCl$_3$): δ 2.33 (s, 6H), 2.36 (s, 3H), 7.17 (s, 2H), 7.52–7.70 (m, 9H), 7.80–7.90 (m, 6H). Other bismuthonium salts were similarly prepared in 88–99% isolated yields. The spectral and analytical data of the newly prepared bismuthonium salts **1c**, **1h**, and **1i** are summarized below, and those of **1a**, **1b**, and **1d–1g** were reported in Refs. 7 and 8.

Tetrakis(4-chlorophenyl)bismuthonium Tetrafluoroborate (1c): Mp 190–192 °C; ^{1}H NMR (CDCl$_3$): δ 7.64 (d, 8H, *J* = 8.4 Hz), 7.71 (d, 8H, *J* = 8.4 Hz); IR ν_{max} 1150–950 (BF$_4^-$); MS (MALDI-TOF) *m/z* 655 ([M − BF$_4$]$^+$). Found: C, 39.06; H, 2.21%. Calcd for C$_{24}$H$_{16}$BBiCl$_4$F$_4$: C, 38.85; H, 2.17%.

Triphenyl(2,6-xylyl)bismuthonium Tetrafluoroborate (1h): Mp 201–203 °C; ^{1}H NMR (CDCl$_3$): δ 2.38 (s, 6H), 7.32–7.40 (m, 3H), 7.56–7.64 (m, 9H), 7.86 (d, 6H, *J* = 7.2 Hz); IR ν_{max} 1150–950 (BF$_4^-$); MS (MALDI-TOF) *m/z* 545 ([M − BF$_4$]$^+$). Found: C, 49.24; H, 3.89%. Calcd for C$_{26}$H$_{24}$BBiF$_4$: C, 49.39; H, 3.83%.

Tris(4-chlorophenyl)mesitylbismuthonium Tetrafluoroborate (1i): Mp >300 °C; ^{1}H NMR (CDCl$_3$): δ 2.32 (s, 6H), 2.37 (s, 3H), 7.18 (s, 2H), 7.60 (d, 6H, *J* = 8.6 Hz), 7.77 (d, 6H, *J* = 8.6 Hz); IR ν_{max} 1150–950 (BF$_4^-$); MS (MALDI-TOF) *m/z*

661 ([M − BF$_4$]$^+$). Found: C, 43.03; H, 3.01%. Calcd for C$_{27}$H$_{23}$BBiCl$_3$F$_4$: C, 43.26; H, 3.09%.

Intermolecular Competition Reactions. TMG (0.020 mmol) was added to a mixture of two kinds of tetraarylbismuthonium salts **1x** and **1y** (0.060 mmol each), geraniol **2** (0.020 mmol), and CH$_2$Cl$_2$ (1.0 mL) at 24 ± 1 °C, and the resulting mixture was stirred at the same temperature. The ratio of arenes produced (Ar[1]H/Ar[2]H) was determined by GC analysis, and the reaction mixture was then concentrated under reduced pressure. The residue was taken up with CDCl$_3$ (ca. 2 mL) and the resulting CDCl$_3$ solution was measured by ^{1}H NMR spectroscopy. Each reaction was carried out three times and the average values of Ar[1]H/Ar[2]H are listed in Table 2. In the competition reactions using **1f–1h**, a trace amount (less than 1%) of benzene was also formed.

Intramolecular Competition Reactions. TMG (0.020 mmol) was added to a mixture of **1d–1i** (0.020 mmol), **2** (0.020 mmol), and CH$_2$Cl$_2$ (1.0 mL) at 24 ± 1 °C. The reaction mixture was worked up and analyzed according to a procedure similar to that described above. Each reaction was carried out three times and the average values are listed in Table 4. The substituent effects listed in Table 3 were determined by taking the number of aryl ligands attached to the bismuth center of **1d–1i** into consideration. That is, the α-hydrogen-abstracting aptitudes listed in Table 3 were calculated based on the ratios of [Ar[1]H]/3[Ar[2]H].

H/D Kinetic Isotope Experiments. TMG (0.010 mmol) was added to a mixture of **1g** (0.010 mmol), *p*-BrC$_6$H$_4$CH$_2$OH (5.6 mg, 0.030 mmol), *p*-BrC$_6$H$_4$CD$_2$OH (5.7 mg, 0.030 mmol), and CDCl$_3$ (1.0 mL) at 24 ± 1 °C. In the intramolecular competition experiments, *p*-BrC$_6$H$_4$CH(D)OH (1.9 mg, 0.010 mmol) was used as the substrate. After 30 min, the reaction mixture was analyzed by ^{1}H NMR spectroscopy, and the ratio of *p*-BrC$_6$H$_4$CHO/*p*-BrC$_6$H$_4$CDO was estimated by the comparison of the integral value of the formyl proton of *p*-BrC$_6$H$_4$CHO with that of the aromatic protons of the two aldehydes. In these reactions, no other products derived from the alcohols were detected. Each reaction was carried out three times and the average values are shown in eqs 1 and 2.

Oxidation of Alcohols by 1g–1i/TMG. TMG (38 mg, 0.33 mmol) was added to a mixture of **1g–1i** (0.33 mmol), alcohol (0.30 mmol), and CH$_2$Cl$_2$ (10 mL), and the resulting mixture was stirred at room temperature. After the alcohol had been consumed (checked by TLC), the reaction mixture was concentrated under reduced pressure to leave an oily residue, which was then subjected on a short silica gel column (hexane–hexane/EtOAc or CH$_2$Cl$_2$). The carbonyl compounds were easily separated from tri-

phenylbismuthane and isolated in a pure form. The yields of volatile carbonyl compounds were determined by ^1H NMR spectra of the reaction mixture.

Chemoselective Oxidation of Primary/Secondary Alcohols. TMG (0.055 mmol) was added to a mixture of two kinds of alcohols (each, 0.055 mmol), oxidant (0.05 mmol), and CDCl$_3$ (1 mL) at 24 ± 1 °C, and the resulting mixture was stirred at the same temperature. The relative ratio of two carbonyl compounds was determined by ^1H NMR spectra of the reaction mixture. Each reaction was carried out twice, and the average values are listed in Table 6.

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9 In most cases, the relative ratio of Ar$^1_3$Bi/Ar$^1_2$Ar^{2}Bi could not be determined accurately due to overlapping of their aromatic protons.

10 Care must be taken to compare the results from the intermolecular competitive experiments of **1a**–**1c** ([Ar$_4$Bi][BF$_4$]) with those of **1f**–**1h** ([Ph$_3$ArBi][BF$_4$]), because the number of ortho/para-substituted aryl ligands attached to the bismuth center is different between these two types of oxidants.

11 The electronic effect observed for the present [Ar$^1_3$Ar^{2}Bi]-[BF$_4$]/TMG system is somewhat larger than that reported for the Ar$^1_2$Ar^{2}BiCl$_2$/DBU system, where the hydrogen-abstracting aptitudes are determined as follows: 4-MeC$_6$H$_4$ (0.92) < C$_6$H$_5$ (1.0) < 4-ClC$_6$H$_4$ (1.1) < 2-MeC$_6$H$_4$ (18) (see, Ref. 5b). The observed electronic effect implies that the α-hydrogen might be abstracted as a hydride in a formal sense.

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