Remarkable Substituent Effects on the Oxidizing Ability of Triarylbismuth Dichlorides in Alcohol Oxidation

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Substituent effects on the oxidizing ability of triarylbismuth dichlorides were examined by intermolecular and intramolecular competition experiments on geraniol oxidation in the presence of DBU. It was found that the oxidizing ability of the dichlorides increases with increasing electron-withdrawing ability of the para substituents, and by introduction of a methyl group at the ortho position of the aryl ligands attached to the bismuth. The intermolecular and intramolecular H/D kinetic isotope effects observed for the competitive oxidation of *p*-bromobenzyl alcohols indicate that the rate-determining step involves C−H bond cleavage. Several primary and secondary alcohols were oxidized efficiently under mild conditions by the combined use of newly developed organobismuth(V) oxidants and DBU.

Pentavalent organobismuth compounds are potential oxidants due to their inherent oxidizing ability derived from the facile Bi^V/Bi^{III} redox process.[1] This property of bismuth has been utilized in alcohol oxidation, where primary and secondary alcohols are oxidized to their corresponding carbonyl compounds by several types of organobismuth(V) reagents.[2] In most cases, however, phenylbismuth(V) compounds of the type Ph_3BiX_2 (X = OH, Cl, Br, OAc, ONO_2, $OBiPh_3Cl$; $X_2 = CO_3$)[2a−f] have been used, and little is known about the relationship between the oxidizing ability and the structure of organyl ligands attached to the bismuth. In 1981, Barton and coworkers reported results of competition experiments on the oxidation of allylic alcohols by Ar_3BiX_2 (X = Cl, Br, ONO_2), in which the relative reactivity of Ar_3BiX_2 was estimated to be in the order: Ar = *p*-tolyl < phenyl < *p*-chlorophenyl < *m*-nitrophenyl.[3] Recently, we found that tri(*o*-tolyl)bismuth dichloride oxidized a variety of alcohols in the presence of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) much more rapidly than triphenylbismuth dichloride and tri(*p*-tolyl)bismuth dichloride.[4] These results suggested to us that more efficient arylbismuth(V) oxidants could be developed by tuning both the electronic and the steric factors of the aryl ligands. Thus, we decided to systematically investigate substituent effects on the oxidizing ability of triarylbismuth dichlorides, and to examine the nature of the transition state of the rate-determining step. The results of the intermolecular and intramolecular competition experiments on the oxidation of alcohols by triarylbismuth dichlorides/DBU are reported here.[5] Oxidation of some alcohols with newly developed oxidants, tris(*p*-trifluoromethylphenyl)bismuth dichloride, tri(*p*-nitrophenyl)bismuth dichloride, and tri(*o*-methyl-*p*-nitrophenyl)bismuth dichloride is also reported.

Results and Discussion

Alcohol oxidation by arylbismuth(V) reagents is considered to proceed through two main steps: formation of an alkoxybismuth(V) intermediate (**A**) and production of a carbonyl compound via α-hydrogen abstraction. In

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(1) (a) Kitchin, J. P. In *Organic Synthesis by Oxidation with Metal Compounds*; Mijs, W. J., De Jonge, C. R. H. I., Eds.; Plenum: New York, 1986; Chapter 15, pp 817−837. (b) Postel, M.; Duñach, E. *Coord. Chem. Rev.* **1996**, *155*, 127. (c) Suzuki, H.; Ikegami, T.; Matano, Y. *Synthesis* **1997**, 249. (d) Komatsu, N. In *Organobismuth Chemistry*; Suzuki, H., Matano, Y., Eds.; Elsevier: New York, 2001; Chapter 5, pp 371−440. (e) Leonard, N. M.; Wieland, L. C.; Mohan, R. S. *Tetrahedron* **2002**, *58*, 8373.

(2) (a) Challenger, F.; Richards, O. V. *J. Chem. Soc.* **1934**, 405. (b) Barton, D. H. R.; Kitchin, J. P.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1978**, 1099. (c) Barton, D. H. R.; Lester, D. J.; Motherwell, W. B.; Papoula, M. T. B. *J. Chem. Soc., Chem. Commun.* **1979**, 705. (d) Barton, D. H. R.; Kitchin, J. P.; Lester, D. J.; Motherwell, W. B.; Papoula, M. T. B. *Tetrahedron* **1981**, *37*, Supplement 9, 73. (e) Dodonov, V. A.; Zinov'eva, T. I.; Osadchaya, N. N. *Zh. Obshch. Khim.* **1988**, *58*, 712. (f) Zinov'eva, T. I.; Dolganova, N. V.; Dodonov, V. A.; Prezhbog, I. G. *Izv. Akad. Nauk. Ser. Khim.* **1998**, 681. (g) Suzuki, H.; Ikegami, T.; Matano, Y. *Tetrahedron Lett.* **1994**, *35*, 8197. (h) Matano, Y.; Nomura, H. *J. Am. Chem. Soc.* **2001**, *123*, 6443. (i) Matano, Y.; Nomura, H.; Suzuki, H.; Shiro, M.; Nakano, H. *J. Am. Chem. Soc.* **2001**, *123*, 10954. (j) Mitsumoto Y.; Nitta, M. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1029.

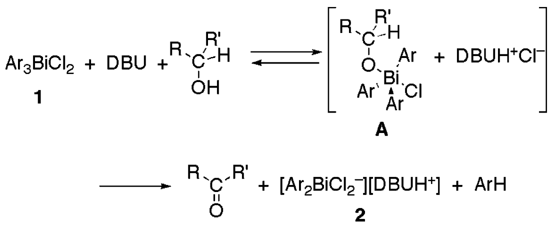
(3) See ref 2d. Potassium carbonate was used as a base. The relative reactivity of Ar_3BiX_2 was determined from the relative ratios of triarylbismuthanes (Ar_3Bi) recovered from the reaction mixture, but significant variation was observed for the yield of Ar_3Bi. Thus, the reported relative rate values are not used here for quantitative discussion.

(4) Matano Y.; Nomura, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3028.

(5) The substituent effects on the arylation of enolizable substrates with triarylbismuth dichlorides were examined. See: (a) Barton, D. H. R.; Bhatnagar, N. Y.; Finet, J.-P.; Motherwell, W. B. *Tetrahedron* **1986**, *42*, 3111. (b) Fedorov, A.; Combes, S.; Finet, J.-P. *Tetrahedron* **1999**, *55*, 1341.

10.1021/jo0485740 CCC: $27.50

SCHEME 1



SCHEME 2

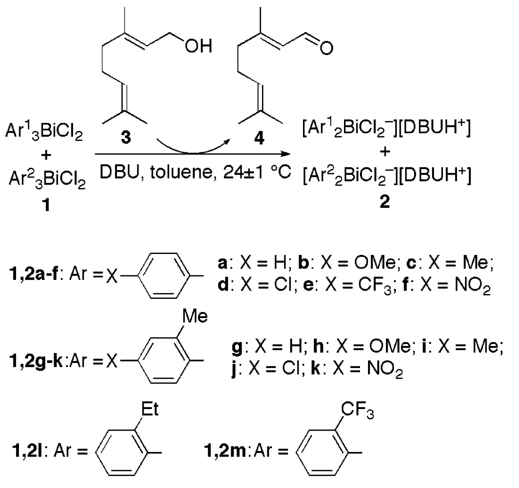


TABLE 1. Competitive Intermolecular Oxidation of 3 with 1a−m

entry	1	2 (rel ratio[a])	entry	1	2 (rel ratio[a])
1	**1a** + **1c**	**2a** + **2c** (80/20)	7	**1g** + **1j**	**2 g** + **2j** (21/79)
2	**1a** + **1d**	**2a** + **2d** (4/96)	8	**1d** + **1g**	**2d** + **2g** (60/40)
3	**1d** + **1e**	**2d** + **2e** (3/97)	9	**1f** + **1k**	**2f** + **2k** (84/16)
4	**1e** + **1f**	**2e** + **2f** (4/96)	10	**1g** + **1*l***	**2g** + **2*l*** (60/40)
5	**1g** + **1h**	**2g** + **2h** (65/35)	11	**1g** + **1m**	**2g** + **2m** (12/88)
6	**1g** + **1i**	**2g** + **2i** (61/39)			

[a] Determined by ^{1}H NMR.

our system using triarylbismuth dichloride (**1**) as an oxidant and DBU as a base, the α-hydrogen is abstracted by the aryl group attached to the bismuth, affording equimolar amounts of carbonyl compound, arene, and ate complex **2** (Scheme 1).[6]

First, we determined the relative oxidizing abilities of triarylbismuth dichlorides by means of competitive intermolecular oxidations, using a series of ortho/para-substituted derivatives **1a**−**m** (Scheme 2). DBU (1.0 equiv) was added to a toluene solution containing geraniol **3** (5×10^{-3} M) and two kinds of dichlorides **1a**−**m** (each 3 equiv) at 24 ± 1 °C. After **3** was oxidized to geranial (**4**), the reaction mixture was concentrated in vacuo and analyzed by ^{1}H NMR spectroscopy. The relative ratios of the two kinds of ate complexes produced (**2a**−**m**, depending on the reactants) were determined from the integral ratios of their aromatic protons (Tables 1 and 2). The relative rates of **1d/1g** and **1f/1k** were found to be 60/40 and 84/16, respectively. On the basis of these results, the relative reactivities of all the dichlorides **1a**−**m** were estimated. As shown in Table 2, the reaction rate increases with increasing electron-withdrawing ability of the para-substituents, and the relative rates for the ortho-unsubstituted series **1a**−**f** are in the following order: Me (0.25) < H (1.0) < Cl (24) ≪ CF_3 (7.7×10^2) ≪ NO_2 (1.9×10^4). A similar electronic effect of the para-substituents was observed for the *o*-Me-substituted series **1g**−**k**: OMe (0.54) < Me (0.63) < H (1.0) < Cl (3.6) ≪ NO_2 (5.8×10^2), although the difference in reactivity is smaller than that observed for the ortho-unsubstituted series **1a**−**f**. In most cases, introduction of the *o*-methyl groups increases the overall rate of the oxidation, and this steric effect becomes more significant as the electron-withdrawing ability of the para-substituents decreases. Thus, **1i** oxidizes **3** about 40 times faster than **1c**, whereas **1j** only oxidizes **3** 2.4 times faster than **1d**. In the case of the *p*-nitro derivatives **1f** and **1k**, introduction of the *o*-methyl group retards the reactivity slightly. We also examined the reactions with other ortho-substituented derivatives **1*l*,m**. The *o*-ethyl derivative **1*l*** oxidized **3** more slowly than the *o*-methyl derivative **1g**, indicating that a suitable size of substituent is necessary for producing the high efficiency. The effect of the trifluoromethyl group is noteworthy. The *p*-CF_3 derivative **1e** oxidized **3** about 3.1×10^3 times faster than the *p*-Me derivative **1c**, whereas the *o*-CF_3 derivative **1m** oxidized **3** only 7 times faster than the *o*-Me derivative **1g**. Thus, the electronic effect of the *o*-trifluoromethyl group on the rate of oxidation is quite different from that of the *p*-trifluoromethyl group.

To evaluate the effects of substituents on the second step, we next carried out competitive intramolecular oxidations using triarylbismuth dichlorides bearing two kinds of aryl groups ($Ar^1_2Ar^2BiCl_2$: **1n**−**u**). This avoids the influence of the first step and enables us to estimate the relative rates at which the aryl groups abstract the α-hydrogen. Compounds **1n**−**u** were prepared by oxidative chlorination of the corresponding triarylbismuthanes with sulfuryl chloride in CH_2Cl_2. Mixed triarylbismuthanes ($Ar^1_2Ar^2Bi$) were prepared from Ar^1_2BiOTf−HMPA complexes and Ar^2MgBr according to the reported procedure.[7] Treatment of **1n**−**u** with **3** in the presence of DBU in toluene at 24 ± 1 °C gave two kinds of ate complexes (Scheme 3). The ratios of unsymmetrical ate complexes **2n**−**u** vs symmetrical ate complexes **2b**−**d**,**g** were determined by ^{1}H NMR spectroscopy. As shown in Tables 2 and 3, the electronic effect of the para-substituents is negligible in comparison to that observed for the intermolecular competition experiments. In contrast, the steric effect on the second step is significant. For example, the *o*-tolyl group of **1u** abstracted the α-hydrogen 16 times faster than the *p*-chlorophenyl group. This is probably because the Bi−C bonds of the alkoxybismuth(V) intermediate bearing the *o*-tolyl groups are weakened due to steric congestion around the bismuth center. The small electronic effect observed, as well as the results from a radical trapping experiment, discards the possibility of any cationic and radical mechanisms.[8,9]

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[6] During the oxidation of 2-propanol with tri(*p*-chlorophenyl)bismuth dichloride/DBU in $CDCl_3$, a type **A** intermediate was observed by ^{1}H NMR spectroscopy: δ 0.98 (d, 6H, *J* = 6.0 Hz, $CHMe_2$), 3.94 (hept, 1H, *J* = 6.0 Hz, $CHMe_2$), 7.62 (d, 6H, *J* = 8.5 Hz, ArH), and 8.28 (d, 6H, *J* = 8.5 Hz, ArH). In the presence or absence of the alcohol, a **1**·DBU type complex was also formed as an equilibrium mixture with **1** and DBU. Thus, the intermediate **A** may be formed via the complex **1**·DBU.

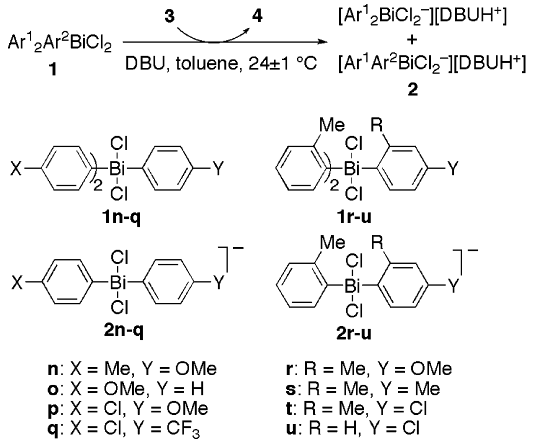
[7] Matano, Y.; Miyamatsu, T.; Suzuki, H. *Organometallics* **1996**, *15*, 1951.

TABLE 2. Substituent Effects Obtained from the Competition Experiments

substituent	inter[a]	intra[b]	substituent	inter[c]	intra[d]
p-OMe		0.46	*o*-Me-*p*-OMe	0.54 (8.6)	0.78 (14)
p-Me	0.25	0.92	*o*-Me-*p*-Me	0.63 (10)	0.63 (11)
p-H	1.0	1.0	*o*-Me-*p*-H	1.0 (16)	1.0 (18)
p-Cl	24	1.1	*o*-Me-*p*-Cl	3.6 (58)	0.67 (12)
p-CF_3	7.8×10^2	1.9			
p-NO_2	1.9×10^4		*o*-Me-*p*-NO_2	5.8×10^2 (3.6×10^3)	
			o-Et	0.67 (11)	
			o-CF_3	7.3 (1.2×10^2)	

[a] Relative reactivity of the dichloride vs **1a**. [b] Relative reactivity of the aryl group vs the phenyl group. [c] Relative reactivity of the dichloride vs **1g**. Values in parentheses are the relative reactivity vs **1a**. [d] Relative reactivity of the aryl group vs the *o*-tolyl group. Values in parentheses are the relative reactivity vs the phenyl group.

SCHEME 3



It is likely that the α-hydrogen is abstracted in a concerted reaction through a weakly polarized, cyclic transition state. Thus, the α-hydrogen-abstracting aptitude of the aryl ligands strongly depends on the bond dissociation energy of the Bi−C bonds of the alkoxybismuth(V) intermediate **A**.

To get some insight into the rate-determining step, we then measured intermolecular and intramolecular H/D kinetic isotope effects for the α-hydrogen abstraction. The intermolecular competition reaction of **1e**,**g** with a mixture of *p*-$BrC_6H_4CH_2OH$ and *p*-$BrC_6H_4CD_2OH$ (each 3 equiv) quantitatively afforded the corresponding aldehydes (eq 1). The isotope effects were determined from ratios of *p*-BrC_6H_4CHO/*p*-BrC_6H_4CDO by means of ^1H NMR spectroscopy. Similarly, the intramolecular isotope effects were estimated by the reaction with *p*-$BrC_6H_4CH(D)OH$ (eq 2). Regardless of the structure of

$$\underset{(R = p\text{-}BrC_6H_4)}{RCH_2OH + RCD_2OH} \xrightarrow[C_6D_6,\ 24\pm1\ ^\circ C]{\mathbf{1e,g} + DBU} \underset{(-\ ArH)}{RCHO} + \underset{(-\ ArD)}{RCDO} \quad (1)$$

$$\mathbf{1e}: k_{H/D} = 3.5\pm0.2;\ \mathbf{1g}: k_{H/D} = 4.5\pm0.4$$

$$\underset{(R = p\text{-}BrC_6H_4)}{RCH(D)OH} \xrightarrow[C_6D_6,\ 24\pm1\ ^\circ C]{\mathbf{1e,g} + DBU} \underset{(-\ ArH)}{RCDO} + \underset{(-\ ArD)}{RCHO} \quad (2)$$

$$\mathbf{1e}: k_{H/D} = 3.5\pm0.2;\ \mathbf{1g}: k_{H/D} = 4.4\pm0.2$$

the aryl ligands, the observed intermolecular kinetic isotope effects are similar to the intramolecular kinetic isotope effects, indicating that the rate-determining step involves α-hydrogen abstraction.[10] The 3- to 4-fold preference for loss of H relative to D observed in the intramolecular competition experiments may support the concerted pathway.[11]

TABLE 3. Competitive Intramolecular Oxidation of 3 with 1n−u

entry	1	2 (rel ratio[a])	entry	1	2 (rel ratio[a])
1	**1n**	**2c** + **2n** (20/80)	5	**1r**	**2g** + **2r** (28/72)
2	**1o**	**2b** + **2o** (52/48)	6	**1s**	**2g** + **2s** (24/76)
3	**1p**	**2d** + **2p** (17/83)	7	**1t**	**2g** + **2t** (25/75)
4	**1q**	**2d** + **2q** (46/54)	8	**1u**	**2g** + **2u** (3/97)

[a] Determined by ^1H NMR.

The substituent effects of the aryl ligands on each step are summarized as follows: (1) The first step is sensitive to the electronic character of the aryl ligands. As the electron-withdrawing ability of the aryl ligands increases, the electrophilicity of the bismuth center is enhanced, which increases the forward rate of the first step. On the other hand, introduction of a methyl group at the ortho position seems to increase the steric congestion around the bismuth center to destabilize the alkoxybismuth intermediates **A** as compared to the starting substrates.[12] As a result, the equilibrium is shifted to the left side. (2) The second step is not susceptible to the electronic character, but rather to the steric character of the aryl ligands. Introduction of a methyl group at the ortho position weakens the Bi−C bonds of **A** due to steric reasons, which increases the rate of α-hydrogen abstraction. Therefore, to construct highly efficient Bi(V) oxidants of the type Ar_3BiX_2, it is desirable to introduce an electron-withdrawing substituent at the para position and/or a moderately bulky substituent like a methyl group at the ortho position by considering a balance between these two effects. In this study, *p*-trifluoromethylphenyl (**1e**), *p*-nitrophenyl (**1f**), and *o*-methyl-*p*-nitrophenyl (**1k**) derivatives were found to be much more effective than the previously reported *o*-tolyl derivative **1g**.

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(8) *Molecular Rearrangements*; de Mayo, P., Ed.; Interscience: New York, 1964; Vol. 1, p 22, and references therein.

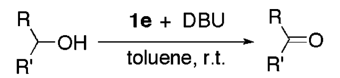
(9) Addition of excess 1,1-diphenylethene did not depress the yield of **4**, ruling out the involvement of free radical species.

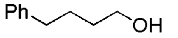
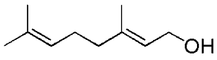
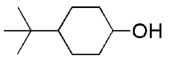
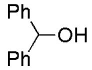
(10) If the first step consists of a slow equilibrium compared to the second step, it would become a rate-determining step. In such a case, however, a small secondary isotope effect should be observed for the intermolecular competition reactions.

(11) In the Swern oxidation of PhCH(D)OH, the intramolecular H/D isotope effect of 2.6 ± 0.3 was observed. See: Marx, M.; Tidwell, T. T. *J. Org. Chem.* **1984**, *49*, 788.

(12) The intermediate **A** derived from the *o*-CF_3 derivative **1m** may be destabilized as compared to the intermediate **A** derived from the *p*-CF_3 derivative **1e** due to the electronic repulsion between the *o*-trifluoromethyl substituents and the alkoxy oxygen atom.

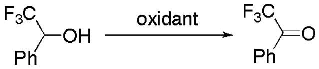
TABLE 4. Oxidation of Alcohols with 1e



	Time/min 1e (1g[b])	Yield/%[a] 1e (1g[b])
	20 (90)	71 (90)
	15 (30)	94 (94)
	20 (120)	95 (93)
	5 (30)	99 (99)

[a] Isolated yield. [b] Data from ref 4.

TABLE 5. Oxidation of 2,2,2-Trifluoro-1-phenylethanol



oxidant (equiv)	reaction conditions	yield/%[a]
1g (1.1)	C_6D_6, rt, 32 h	98[b]
1e (1.1)	$CDCl_3$, rt, 50 min	>95
1f (1.1)	$CDCl_3$, rt, 5 min	>95
1k (1.1)	$CDCl_3$, rt, 5 min	>95
Dess−Martin (3.7)	CH_2Cl_2, rt, 3 h	76[c]

[a] NMR yield. [b] Data from ref 4. [c] Data from ref 14a. Isolated yield.

With new bismuth(V) oxidants **1e**,[13] **1f**,[5] and **1k** in hand, we examined the oxidation of some primary and secondary alcohols. The reaction times and yields are summarized in Tables 4 and 5, together with those reported for **1g**. As expected, the oxidation with **1e** proceeded more rapidly than that with **1g** in all cases. It is noteworthy that 2,2,2-trifluoro-1-phenylethanol can be rapidly oxidized by **1e**,**f**,**k** to the corresponding trifluoromethyl ketone at room temperature.[14] The efficiency of this oxidation is higher than that of the Dess−Martin oxidation[14a] (Table 5).

In summary, we systematically examined the substituent effects on the oxidizing ability of triarylbismuth dichlorides by the competition experiments on geraniol oxidation in the presence of DBU. Highly efficient Bi(V) oxidants of the type Ar_3BiX_2 were developed successfully by introducing an electron-withdrawing substituent at the para position and/or a methyl group at the ortho position.

Experimental Section

Compounds. Triarylbismuth dichlorides **1** were prepared from the corresponding triarylbismuthanes and sulfuryl chloride as described below. *p*-Bromobenzyl alcohol-α-d[15] and *p*-bromobenzyl alcohol-α,α-d_2[16] were prepared by reduction of *p*-bromobenzaldehyde and *p*-bromobenzoic acid ethyl ester, respectively, with $LiAlD_4$. DBU was purified by distillation. Other reagents were used as commercially received.

Triarylbismuth Dichlorides 1. General procedure: Sulfuryl chloride (0.44 mL, 5.5 mmol) was added to a CH_2Cl_2 solution (30 mL) of triarylbismuthane (5.0 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature, and gently refluxed for 2−3 h for the substrates bearing the ortho-substituents or the para-electron-withdrawing substituents. The resulting mixture was evaporated under reduced pressure to leave a colorless or pale yellow solid, which was recrystallized from CH_2Cl_2/hexane to give triarylbismuth dichloride **1**. New compounds were characterized by ^1H NMR, FABMS, and elemental analyses, and the data are summarized in the Supporting Information.

Intermolecular Competition Reactions. A toluene solution of DBU (0.10 M × 0.20 mL, 0.020 mmol) was added to a mixture of two kinds of triarylbismuth dichlorides **1a**−**j** (0.060 mmol each), **3** (0.020 mmol), and toluene (2 mL) at 24 ±1 °C. The mixture was stirred for 0.5−3 h at the same temperature, and the resulting mixture was concentrated under reduced pressure. The residue was taken up with $CDCl_3$ (ca. 2 mL) and the resulting $CDCl_3$ solution was measured immediately by ^1H NMR spectroscopy. Each reaction was carried out three times and the average values are listed in Table 1. Due to the low-yield formation of **2b** as compared to **2a**,**c**, the reliable data could not be obtained for the reaction with use of **1b** and **1a**,**c**. The signals due to **2a**−**m** were assigned by comparison with authentic specimen observed independently. The ^1H NMR data of **2a**−**m** are summarized in the Supporting Information.

Intramolecular Competition Reactions. A toluene solution of DBU (0.10 M × 0.20 mL, 0.020 mmol) was added to a mixture of **1k**−**r** (0.020 mmol), **2** (0.020 mmol), and toluene (4 mL) at 24 ± 1 °C. The reaction mixture was worked up and analyzed by ^1H NMR spectroscopy as described above. Each reaction was carried out three times and the average values are listed in Table 3. The ^1H NMR data of **2n**−**u** are summarized in the Supporting Information.

H/D Kinetic Isotope Experiments. A C_6D_6 solution of DBU (0.50 M × 0.020 mL, 0.010 mmol) was added to a mixture of **1e**,**g** (0.010 mmol), *p*-$BrC_6H_4CH_2OH$ (0.030 mmol), *p*-$BrC_6H_4CD_2OH$ (0.030 mmol), and C_6D_6 (1 mL) at 24 ± 1 °C. In the intramolecular competition experiments, *p*-$BrC_6H_4CH(D)OH$ (0.010 mmol) was used as the substrate. After 15−20 min, the reaction mixture was analyzed by ^1H NMR spectroscopy, and the ratio of *p*-BrC_6H_4CHO/*p*-BrC_6H_4CDO was estimated by comparing the integral value of the formyl proton of *p*-BrC_6H_4CHO 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 1e/DBU. DBU (46 mg, 0.30 mmol) was added to a mixture of **1e** (0.30 mmol), alcohol (0.27 mmol), and toluene (3 mL), and the resulting mixture was stirred at room temperature. After the alcohol had been consumed (checked by TLC), the precipitates were filtered off through a thin Celite bed. The filtrate was concentrated under reduced pressure to leave an oily residue, which was then passed through a short silica gel column (ca. 50 mL of hexane/EtOAc as eluent) to afford the carbonyl compound. The reaction proceeded similarly on a larger scale (1.0−2.0 mmol of alcohol). In the reaction of 4-phenyl-1-butanol, 4-phenylbutanal was formed in a good NMR yield (ca. 90%) with a small amount of byproduct bearing a formyl group.

Oxidation of 2,2,2-Trifluoro-1-phenylethanol by 1e,f,k/DBU. DBU (0.030 mmol) was added into an NMR tube

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containing a mixture of **1e** (0.030 mmol), 2,2,2-trifluoro-1-phenylethanol (0.027 mmol), and $CDCl_3$ (1.0 mL), and the resulting mixture was shaken quickly at room temperature. The mixture was then monitored by ^1H NMR at several intervals, revealing that α,α,α-trifluoroacetophenone was formed in a good conversion yield. The reactions with **1f** and **1g** were similarly performed, where the starting alcohol was consumed within 5 min.

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Supporting Information Available: Spectral and analytical data for **1h**−**u** and ^1H NMR data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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