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Fluorotetraphenylbismuth: A New Reagent for Efficient Regioselective α-Phenylation of Carbonyl Compounds

Takashi Ooi, Ryoji Goto, and Keiji Maruoka*

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-8502, Japan

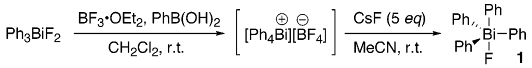
Received March 4, 2003; E-mail: maruoka@kuchem.kyoto-u.ac.jp

Largely through the pioneering work of Barton and co-workers, the synthetic utility of polyarylbismuth(V) compounds as arylating and oxidizing agents has been illuminated[1] and occupies an important place in organic synthesis.[2] Tetraphenylbismuth(V) compounds (Ph_4BiX) are a representative reagent for the phenylation of various organic molecules, and tetraphenylbismuth carboxylates (X = OCOR; R = CH_3, CF_3, etc.) and sulfonates (X = OSO_2R; R = *p*-CH_3Ph, CF_3, etc.) are often employed mainly because of their adequate reactivity and thermal stability tuned by the weakly coordinating (less nucleophilic) anions (X).[3] However, tetraphenylbismuth(V) compounds with a strongly coordinating (highly nucleophilic) anion such as chloro- or bromotetraphenylbismuths are known to decompose rapidly to yield triphenylbismuthine (Ph_3Bi) and the corresponding halobenzenes (PhX) in the solid state at room temperature.[4] Hence, there have been no well-characterized examples, and their synthetic utility has remained to be explored. We report herein the first synthesis of fluorotetraphenylbismuth (**1**), which is thermally stable and structurally characterized by X-ray crystallography. Taking advantage of its unique amphiphilic property of possessing both nucleophilic and electrophilic moieties within a molecule, **1** has been successfully utilized for the efficient regioselective α-phenylation of ketones and esters. The selective α-alkenylation of carbonyl compounds based on this approach is also reported.

The $BF_3{\cdot}OEt_2$-promoted reaction of triphenylbismuth difluoride (Ph_3BiF_2) with phenylboronic acid in CH_2Cl_2 cleanly produced tetraphenylbismuthonium tetrafluoroborate,[5] and subsequent one-pot anion exchange by treatment with cesium fluoride (CsF, 5 equiv) in acetonitrile at room temperature afforded the requisite fluorotetraphenylbismuth (**1**), which was easily purified by recrystallization from CH_2Cl_2/hexane (80%). Surprisingly, **1** was found to be thermally stable in the solid state despite the presence of both the electrophilic phenyl group and the nucleophilic fluorine atom on the central bismuth.[6,7] Single-crystal X-ray diffraction analysis revealed that the bismuth center of **1** adopts a distorted trigonal bipyramidal geometry with three *ipso* carbons at the equatorial sites and one *ipso* carbon and fluorine atom at the apical sites (Figure 1).[7−9] Indeed, the Bi−C_{ap} bond length (2.260(6) Å) is longer than that of the Bi−C_{eq}. The Bi−F bond length is 2.218(3) Å, which is shorter than the Bi−F bond of Ph_3BiF_2 over 0.3 Å.[10]

Taking the unique amphiphilic property of **1** as well as the high affinity of fluorine toward silicon atom into consideration,[11] we examined the α-phenylation of ketones by the combination of **1** and enol silyl ethers (Scheme 1). Remarkably, mixing of **1** and 1-trimethylsiloxy-3,4-dihydronaphthalene in THF at −40 °C and stirring at room temperature for 10 min gave rise to 2-phenyl-1-tetralone almost quantitatively without formation of the polyphenylated products (entry 1 in Table 1).

Other representative examples listed in Table 1 unequivocally demonstrate the efficiency and generality of this simple α-phenylation system. The following characteristic features have been noted.[12] (1) The reaction was generally completed within 1 h at room temperature, and the α-monophenylated product was obtained in excellent chemical yield even in the case with the substrate having no α-substituent, indicating that **1** is far superior to the previously known diaryliodonium fluorides.[13] (2) The regiochemistry was rigorously governed by the enol silyl ethers employed as exemplified by the reactions of 2-methylcyclohexanone derivatives (entries 4 and 5).[14] (3) Facile construction of α-quaternary carbon centers was certainly feasible under similar conditions (entries 5, 9, and 11). (4) Selective α-phenylation of esters was also achieved by using ketene silyl acetals as substrates (entries 10 and 11). As was also illustrated in Scheme 1, the reaction would be initiated by the nucleophilic attack of fluorine on the silicon atom of enol silyl ether, generating either *C*- or *O*-tetraphenylbismuth intermediate with the liberation of Me_3SiF.[15] The subsequent ligand coupling process then led to the formation of the α-phenylation product.



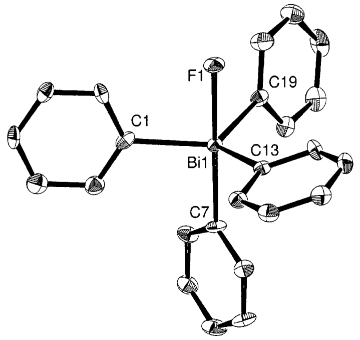
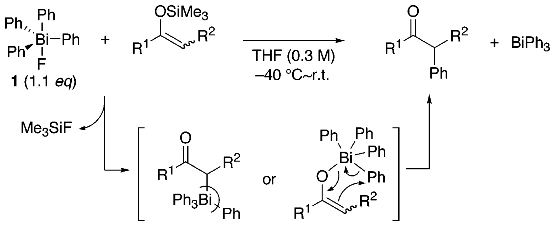


Figure 1. ORTEP diagram of Ph_4BiF (**1**). Bi−F, 2.218(3); Bi−C(1), 2.214(6); Bi−C(7), 2.260(6); Bi−C(13), 2.199(6); Bi−C(19), 2.202(6); F−Bi−C(7), 179.1(2); F−Bi−C(1), 83.6(2); F−Bi−C(13), 81.9(2); F−Bi−C(19), 82.5(2); C(1)−Bi−C(7), 96.8(2); C(7)−Bi−C(13), 97.2(2); C(7)−Bi−C(19), 97.9(2); C(1)−Bi−C(13), 116.2(2); C(1)−Bi−C(19), 123.2(2); C(13)−Bi−C(19), 115.8(2).

Scheme 1



Our approach was further extended to the selective α-alkenylation of carbonyl compounds.[16,17] For instance, fluoro(2-phenylethenyl)-tris(*p*-tolyl)bismuth (**2**) was readily prepared in a similar manner from the corresponding tetrafluoroborate,[5] and simple treatment of 1-trimethylsiloxy-3,4-dihydronaphthalene with **2** in THF at −40 °C for 30 min resulted in the selective transfer of the 2-phenyl-

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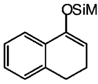
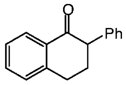
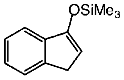
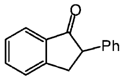
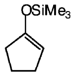
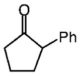
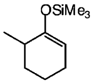
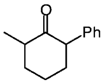
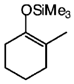
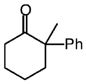
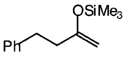
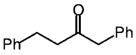
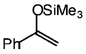
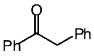
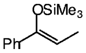
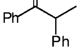
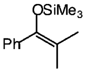
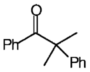
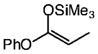
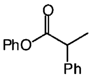
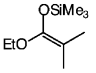
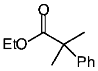
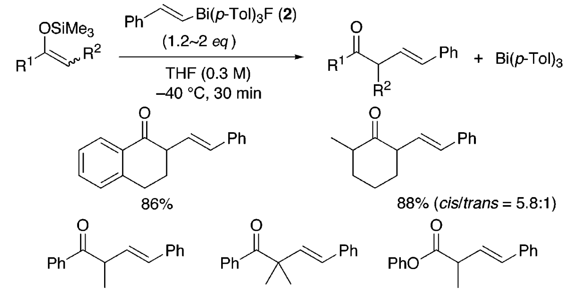
Table 1. Regioselective Phenylation of Enol Silyl Ethers and Ketene Silyl Acetals with Ph_4BiF (**1**)[a]

entry	substrate	react. time (h)	product	% yield[b]
1		0.2		99
2		0.2		92
3		0.2		92
4		1		92
5		2.5		90
6		0.2		90
7		0.2		96
8		0.2		97
9		1		98
10		0.5		85
11		1		83

[a] The reaction was carried out with 1.1 equiv of Ph_4BiF (**1**) in THF (0.3 M) from −40 °C to room temperature. See the Supporting Information. [b] Isolated yield.

Scheme 2



ethenyl moiety, producing the desired β,γ-unsaturated ketone in 86% isolated yield (Scheme 2). Here, neither the transfer of *p*-tolyl group nor the isomerization of olefin was observed, and the generality of this system was quite obvious by the selected examples shown in Scheme 2.

In conclusion, we have synthesized and characterized fluorotetraphenylbismuth for the first time. Contrary to the previous common understanding of this type of organobismuth(V) compounds, **1** was found to be thermally stable, maintaining its amphiphilic property. Hence, **1** can be used as an off-the-shelf reagent in organic synthesis, and its utility has been clearly demonstrated in applications to the efficient α-phenylation of ketones and esters. Moreover, applicability of the present approach to the selective α-alkenylation of carbonyl compounds was exemplified by the use of **2** as a representative reagent. These results also imply the vast potential of organobismuth(V) compounds of type **1** and **2** as useful precursors of a wide variety of pentavalent organobismuth compounds based on the utilization of the eminent fluorine−silicon interaction or the inherent basicity of the fluorine atom.

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Supporting Information Available: Representative synthetic procedure and physical characterization of **1**, **2**, and all new compounds (PDF); the crystallographic data for **1** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) When heated at 100 °C for 5 min, no decomposition was observed. Upon further heating at its melting point (135 °C) for 2 min, **1** decomposed partially (ca. 20%), and the formation of triphenylbismuthine and fluorobenzene was detected by ^{1}H NMR.

(7) This is in sharp contrast to tetrakis(2-methoxyphenyl)bismuthonium halides (Cl, Br, and I) which are highly stabilized through the intramolecular coordination of the methoxy oxygen toward the bismuth center adopting a tetrahedral geometry. A large separation between the bismuth and halogen atoms was observed in these ionic compounds. See: Suzuki, H.; Ikegami, T.; Azuma, N. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1609.

(8) Crystal structure data for **1** collected at 123 K: $C_{24}H_{20}FBi$, $M_w = 536.40$, triclinic, space group *P*-1, $a = 9.431(2)$, $b = 10.027(2)$, $c = 11.824(1)$ Å, $\alpha = 107.336(5)°$, $\beta = 90.416(8)°$, $\gamma = 113.695(5)°$, $V = 967.0(3)$ Å^3, $Z = 2$, $D_{calcd} = 1.842$ gcm^{-3}, $R_1 = 0.032$.

(9) ^{13}C NMR analysis of **1** in $CDCl_3$ at room temperature revealed that each phenyl group was equivalent in solution. See the Supporting Information.

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(14) Attempted reaction of 2-methylcyclohexanone with NaH (1.1 equiv) and tetraphenylbismuthonium tetrafluoroborate (1.1 equiv) in THF (0.3 M) at room temperature for 72 h resulted in the formation of 2-methyl-6-phenylcyclohexanone (5%, *cis*/*trans* mixture), 2-methyl-2-phenylcyclohexanone (18%), and 2-methyl-6,6-diphenylcyclohexanone (11%).

(15) An ^{19}F NMR study of an equimolar mixture of **1** and 1-trimethylsiloxy-3,4-dihydronaphthalene in THF-d_8 at room temperature showed the appearance of the signal of trimethylsilyl fluoride at δ −154.21 ppm.

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