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First synthesis of alkynyltriphenylbismuthonium salts and their dual reaction modes in sulfonylation

Yoshihiro Matano*

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan.
E-mail: matano@kuchem.kyoto-u.ac.jp

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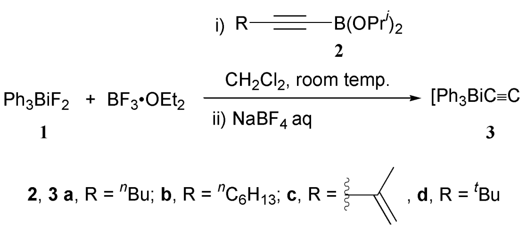
Treatment of triphenylbismuth difluoride with alkynyldiisopropoxyboranes in the presence of $BF_3·OEt_2$ in CH_2Cl_2 gives alkynyltriphenylbismuthonium tetrafluoroborates, which react with sodium *p*-toluenesulfinate in dual reaction modes depending on the solvents employed.

The chemistry of onium salts with an acetylenic group on the cationic heteroatom constitutes an attractive area of study in terms of both heteroatom and acetylene chemistry.[1] In general, three reaction sites are conceivable for this class of compounds: the heteroatom center, the acetylenic α-carbon and the acetylenic β-carbon. Owing to this diversity, such compounds have recently been utilized as versatile reagents in organic synthesis.[1] However, no information is yet available for alkynylbismuthonium salts owing to the lack of a general method for constructing a Bi–C_{sp} bond. Recently, the Lewis acid-promoted reactions of triarylbismuth difluorides with organometallic reagents have proven to be efficient methods for the preparation of various types of bismuthonium salts bearing a Bi–C_{sp^3} or Bi–C_{sp^2} bond ($[Ar_3BiR^+][X^-]$; R = alkyl, alkenyl, aryl).[2] Owing to the high leaving ability of the triarylbismuthonio group, this class of compounds has been shown to have unique reactivities that differ significantly from those of lighter element counterparts. These results have led me to disclose the nature of the Bi–C_{sp} bond in bismuthonium salts. Reported here are the first synthesis, crystal structure and reactions of alkynyltriphenylbismuthonium salts.

As shown in Scheme 1, alkynyltriphenylbismuthonium tetrafluoroborates **3a–d** were prepared by the reaction of triphenylbismuth difluoride **1** with the corresponding alkynyldiisopropoxyboranes **2a–d**[3,4] in the presence of $BF_3·OEt_2$ (Table 1).† No Bi–C_{sp} coupling took place in the absence of the Lewis acid, as was observed in the reaction of **1** with other types of organoboronic acids.[2f,g] Compounds **3** were isolated as colorless solids in 88–93% yields by recrystallization from CH_2Cl_2–Et_2O and characterized by NMR, IR and mass spectrometry.



Scheme 1

Table 1 Alkynyltriphenylbismuthonium tetrafluoroborates **3**

Entry	3	Yield (%)	Mp/°C
1	**3a** ($[Ph_3Bi^+C\equiv C^nBu][BF_4^-]$)	88	137–138
2	**3b** ($[Ph_3Bi^+C\equiv C^nC_6H_{13}][BF_4^-]$)	93	83–85
3	**3c** ($[Ph_3Bi^+C\equiv CC(Me)=CH_2][BF_4^-]$)	89	139–141
4	**3d** ($[Ph_3Bi^+C\equiv C^tBu][BF_4^-]$)	90	160–161

The structure of **3d** was further determined by X-ray crystallography (Fig. 1).‡ The bismuth center of **3d** adopts a pseudotrigonal bipyramidal (TBPY) geometry with three phenyl *ipso* carbons at the equatorial sites and an acetylenic α carbon and a fluorine atom at the apical sites. The Bi···F(1) distance of 2.749(4) Å is longer than the sum of their covalent radii (2.10 Å) but much shorter than the sum of their van der Waals radii (3.75 Å),[5] indicating that the tetrafluoroborate anion interacts strongly with the cationic bismuth center. Owing to this interaction, the B–F(1) bond is slightly longer than other B–F bonds. The TBPY geometry observed for **3d** may be attributable to the steric as well as electronic character of the acetylenic group: known alkyl-, alkenyl- and aryl-triphenylbismuthonium tetrafluoroborates all adopt a distorted tetrahedral geometry with the spatially separated BF_4^- anion.[2a,b,d,f,g] The Bi–C(1) bond length [2.151(8) Å] is slightly shorter than the Bi–C_{Ph} bond lengths [2.179(9)–2.235(9) Å], reflecting the difference in electronic properties between the C_{sp} and C_{sp^2} atoms. The C(1)–C(2) bond length [1.19(1) Å] is almost identical to that of a typical C≡C triple bond (1.20 Å), and the acetylenic moiety is bent slightly at the C(1) atom. Although the reason for this bent conformation is not clear at present, it might be due to the steric effect caused by the neighboring molecules. In $CDCl_3$, the *ortho* protons of the phenyl groups of **3** were observed at relatively lower field (*δ* 8.25) than those of tetrahedral bismuthonium salts (*δ* 7.7–7.8), suggesting that the TBPY geometry of **3** is also maintained in solution.

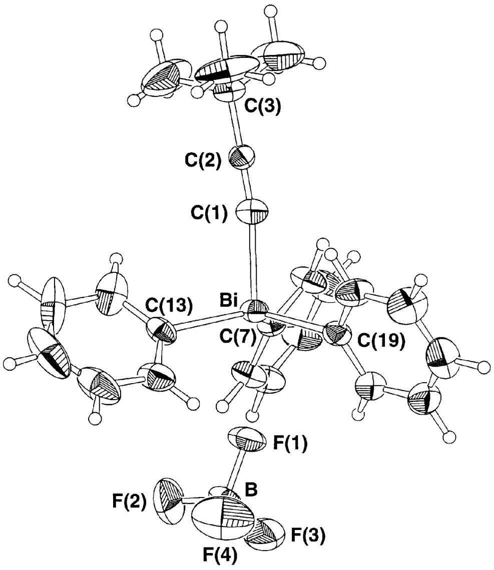


Fig. 1 ORTEP diagram (30% probability ellipsoids) of **3d**. Selected bond lengths (Å) and angles (°): Bi–C(1) 2.151(8), Bi–C(7) 2.210(8), Bi–C(13) 2.235(9), Bi–C(19) 2.179(9), B–F(1) 1.38(1), B–F(2–4) 1.29(1)–1.33(1), C(1)–C(2) 1.19(1), C(2)–C(3) 1.47(1), Bi···F(1) 2.749(4); C(1)–Bi–C(7) 100.1(3), C(1)–Bi–C(13) 98.6(3), C(1)–Bi–C(19) 102.6(3), C(7)–Bi–C(13) 122.1(3), C(7)–Bi–C(19) 111.9(3), C(13)–Bi–C(19) 116.4(3), Bi–C(1)–C(2) 170.9(8), C(1)–C(2)–C(3) 178.6(10).

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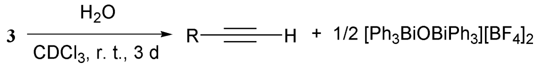
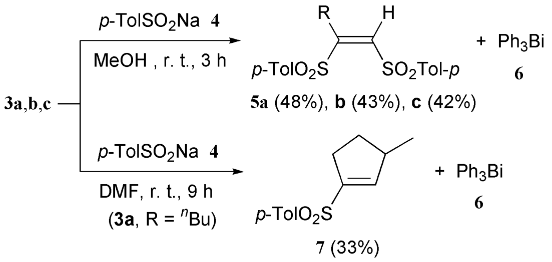
Alkynylbismuthonium salts **3** were slowly hydrolyzed in open air or in wet solution to give μ-oxobis(triphenylbismuth) bis(tetrafluoroborate)[2a] and parent acetylenes (Scheme 2). Thus, it is reasonable to assume that the hydroxy group of water is bound to the bismuth atom. This mode of hydrolysis is in marked contrast to that observed for methyltriphenylbismuthonium tetrafluoroborate, which produces methanol, triphenylbismuthine and fluoroboric acid.[2g] In this case, the hydroxy group is bound to the methyl group. These two results reflect the difference in reactivity between the Bi–C_{sp} and Bi–C_{sp^3} bonds in bismuthonium salts.



$$\mathbf{3}\ \xrightarrow[\text{CDCl}_3\text{, r. t., 3 d}]{H_2O}\ R{-}C{\equiv}C{-}H\ +\ 1/2\ [Ph_3BiOBiPh_3][BF_4]_2$$

Scheme 2

The reaction of alkynyltriphenylbismuthonium salts **3** with a sulfinate anion was examined (Scheme 3). The treatment of **3a** with 2 equiv. of sodium *p*-toluenesulfinate **4** in MeOH afforded (*Z*)-1,2-bis(*p*-toluenesulfonyl)hex-1-ene **5a** (R = ^{n}Bu) in 48% yield together with triphenylbismuthine **6**.§ The (*Z*)-configuration of **5a** was determined by comparison with the spectral properties of analogous compounds[6] as well as by NOE experiment. Compounds **3b** and **3c** also reacted with **4** in MeOH to give the corresponding disulfones **5b** (R = $^nC_6H_{13}$, 43%) and **5c** [R = C(Me)=CH_2, 42%], respectively, with good recovery of **6**. By contrast, when a similar reaction of **3a** was carried out in DMF, 1-sulfonyl-3-methylcyclopentene **7** was obtained as a major product (33%) and **5a** was not formed at all.§



Scheme 3

Plausible mechanisms for the sulfonylations of **3a** are depicted in Scheme 4. The initial stage in both reactions would be a Michael addition of the sulfinate anion to the β-alkynyl carbon. In MeOH, the resulting ylide **8** would be protonated to produce an alkenylbismuthonium intermediate **9**, which subsequently reacts with the sulfinate anion to give **5** with retention of the configuration.[2d] In DMF, ylide **8** would eliminate bismuthine **6** to generate an alkylidene carbene intermediate **10**, which undergoes 1,5-C–H insertion to give cyclopentene **7**. Similar types of tandem bis-sulfonylation and sulfonylation/C–H insertion reactions were reported for alkynylselenonium[7] and alkynyliodonium salts,[8] respectively. Interestingly, alkynylbismuthonium salts **3** react with the same nucleophile *via* two different pathways depending on the solvents employed.

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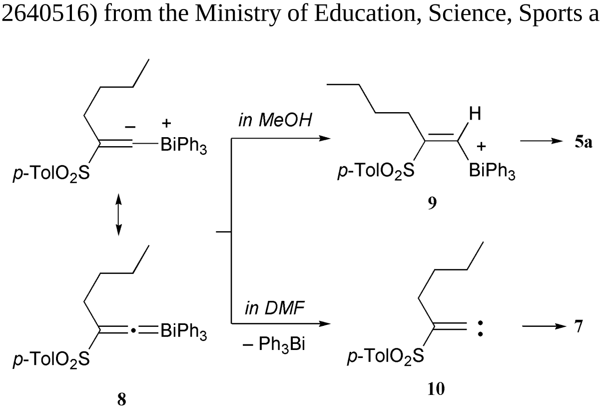

Scheme 4

Notes and references

† *A typical example:* to a mixture of **1** (1.17 g, 2.44 mmol), $BF_3 \cdot OEt_2$ (0.35 cm^3, 2.7 mmol) and CH_2Cl_2 (10 cm^3) was added **2a** (858 mg, 3.00 mmol) at 0 °C. The resulting solution was stirred at room temp. After 15 h, an aqueous solution (10 cm^3) of $NaBF_4$ (2.2 g, 20 mmol) was added, and the resulting two-phase solution was vigorously stirred for 1 min. The organic phase was separated, dried over $MgSO_4$ and concentrated under reduced pressure to leave an oily residue, which was recrystallized from Et_2O–CH_2Cl_2 (10 : 1) to afford **3a** as a colorless crystalline solid (1.31 g, 88%): δ_H 0.96 (t, 3H, *J* 7.2), 1.36–1.74 (m, 4H), 2.48 (t, 2H, *J* 7.0), 7.52–7.75 (m, 9H), 8.25 (d, 6H, *J* 7.8); IR ν_{max} 2147 (C≡C), 1200–1000 (BF_4^-) cm^{-1}; FABMS *m/z* 521 [M – BF_4]$^+$. Found: C, 47.46; H, 4.09. $C_{24}H_{24}BBiF_4$ requires C, 47.39; H, 3.98%. **3b**: δ_H 0.90 (t, 3H, *J* 6.5), 1.20–1.75 (m, 8H), 2.48 (t, 2H, *J* 6.9), 7.53–7.80 (m, 9H), 8.25 (d, 6H, *J* 7.6); IR ν_{max} 2151 (C≡C), 1200–1000 (BF_4^-) cm^{-1}; FABMS *m/z* 549 [M − BF_4]$^+$. Found: C, 48.19; H, 4.37. $C_{26}H_{28}BBiF_4$ requires C, 49.08; H, 4.44%. **3c**: δ_H 2.00 (s, 3H), 5.51 (s, 1H), 5.60 (s, 1H), 7.50–7.80 (m, 9H), 8.25 (d, 6H, *J* 7.2); IR ν_{max} 2130 (C≡C), 1200–900 (BF_4^-) cm^{-1}; FABMS *m/z* 505 [M − BF_4]$^+$. Found: C, 46.53; H, 3.32. $C_{23}H_{20}BBiF_4$ requires C, 46.65; H, 3.40%. **3d**: δ_H 1.37 (s, 9H), 7.59 (t, 3H, *J* 7.2), 7.68 (t, 6H, *J* 7.6), 8.24 (d, 6H, *J* 7.6); IR ν_{max} 2130 (C≡C), 1200–1000 (BF_4^-) cm^{-1}; FABMS *m/z* 521 [M − BF_4]$^+$. Found: C, 47.25; H, 4.01. $C_{24}H_{24}BBiF_4$ requires C, 47.39; H, 3.98%.

‡ The crystal structure of **3d** consists of two isolated molecules which differ little from each other as to the configuration of the central bismuth atom. The ORTEP diagram and selected bond parameters in Fig. 1 are those of the selected molecule. *Crystal data*: $C_{48}H_{48}B_2Bi_2F_8$, M = 1216.48, monoclinic, a = 17.863(1), b = 13.7651(8), c = 19.835(1) Å, β = 98.235(2)°, V = 4826.8(5) Å^3, T = 296 K, space group $P2_1/a$ (no. 14), Z = 4, D_c = 1.674 g cm^{-3}, μ(Mo-Kα) = 73.30 cm^{-1}, 40421 reflections measured, 10596 unique (R_{int} = 0.057) refined to R_w = 0.108, R_1 = 0.039 [I > 2.0σ(I)]. CCDC 182/1812. See http://www.rsc.org/suppdata/cc/b0/b006881k/ for crystallographic files in .cif format.

§ **5a**: Mp 61–62 °C; δ_H 0.83 (t, 3H, *J* 6.9), 1.10–1.22 (m, 4H), 2.39 (t, 2H, *J* 7.6), 2.46 (s, 6H), 6.72 (s, 1H), 7.36 (d, 4H, *J* 8.1), 7.92 (d, 2H, *J* 8.1), 7.97 (d, 2H, *J* 8.1); FABMS *m/z* 393 [M + 1]$^+$. Found: C, 61.26; H, 6.26. $C_{20}H_{24}O_4S_2$ requires C, 61.20; H, 6.16%. Satisfactory spectroscopic and analytical data are available for **5b**,**c**. **7**: δ_H 1.08 (d, 3H, *J* 7.1), 1.55 (m, 1H), 2.23 (m, 1H), 2.44 (s, 3H), 2.45–2.63 (m, 2H), 2.92 (m, 1H), 6.58 (dd, 1H, *J* 1.7, 3.8), 7.33 (d, 2H, *J* 8.0), 7.77 (d, 2H, *J* 8.0); FABMS *m/z* 237 [M + 1]$^+$.

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