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A New and Efficient Method for the Preparation of Bismuthonium and Telluronium Salts Using Aryl- and Alkenylboronic Acids. First Observation of the Chirality at Bismuth in an Asymmetrical Bismuthonium Salt

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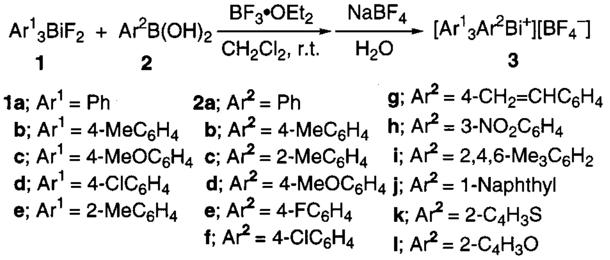
Summary: Treatment of triarylbismuth difluorides with aryl- and alkenylboronic acids in the presence of BF_3·OEt_2 afforded tetraaryl- and alkenyltriarylbismuthonium tetrafluoroborates, respectively, while similar treatment of diphenyltellurinyl difluoride yielded the corresponding telluronium salts. The chirality at bismuth was observed for the first time from the ^{1}H NMR spectrum of an asymmetrical bismuthonium salt.

Onium salts derived from heavy main-group elements have been receiving increasing interest owing to their unique properties and reactivity.[1] Among the reported methodologies for the synthesis of this class of compounds, the reaction between a hypervalent compound of the type R_nMX_2 (M = Bi, Te, I, etc.; X = anionic species) and an organometallic reagent provides the most reliable preparation of a variety of carbon−heteroatom bonds leading to onium salts. Recently, we reported a convenient method for the synthesis of alkyl- and alkenyltriarylbismuthonium salts based on the Lewis-acid-promoted reaction of triarylbismuth difluorides with the corresponding organosilanes and/or -stannanes.[2] Although a similar reaction using arylstannanes could also lead to unsymmetrical tetraarylbismuthonium salts, comparatively severe conditions were needed for the Bi−C_{aryl} coupling and the aryl ligands transferable to the bismuth were limited to the electron-rich ones.[3] To overcome these limitations, we have investigated arylboronic acids,[4] which are well-established as useful aryl transfer reagents in organic synthesis.[5] Rather unexpectedly, a literature search showed that these reagents find at present only limited use in the preparation of onium salts bearing an aryl ligand.[6]

Scheme 1



We report herein a new and efficient method for the preparation of aryl- and alkenylbismuthonium salts by the BF_3·OEt_2-promoted reaction of triarylbismuth difluorides with aryl- and alkenylboronic acids. The method has been successfully applied to the synthesis of an asymmetrically tetraarylated bismuthonium salt, and the chirality at tetrahedral bismuth center was studied by means of ^{1}H NMR spectroscopy.

As is shown in Scheme 1, treatment of triarylbismuth difluorides **1** with arylboronic acids **2** in the presence of BF_3·OEt_2 in CH_2Cl_2 at room temperature afforded the corresponding symmetrical and unsymmetrical tetraarylbismuthonium tetrafluoroborates **3** in the yields listed in Table 1.[7] Onium salts **3** were isolated in a high state of purity by simple recrystallization from CH_2Cl_2−Et_2O (1:10) after aqueous workup.[8]

Aryl ligands bearing either an electron-donating or electron-withdrawing substituent were both transferable with ease (entries 1−6). The vinyl group remained intact throughout the reaction (entry 7). When an excess of the Lewis acid and the compound **2h** were used, the 3-nitrophenyl group also could be transferred

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(1) Recent reviews: (a) Huang, Y. Z.; Shi, L. L.; Yang, J. H.; Xiao, W. J.; Li, S. W.; Wang, W. B. In *Heteroatom Chemistry*; Block, E., Ed.; VCH: New York, 1990; p 189. (b) Huang, Y.-Z. *Acc. Chem. Res.* **1992**, *25*, 182. (c) Matano, Y.; Suzuki, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2673. (d) Shimizu, T.; Kamigata, N. *Yuki Gosei Kagaku Kyokaishi* **1997**, *55*, 35. (e) Moriarty, R. M.; Vaid, R. K. *Synthesis* **1990**, 431. (f) Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 274. (g) Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996**, *96*, 1123. (h) Varvoglis, A. *Tetrahedron* **1997**, *53*, 1179. (i) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502 and references therein.

(2) (a) Matano, Y.; Azuma, N.; Suzuki, H. *Tetrahedron Lett.* **1993**, *34*, 8457. (b) Matano, Y.; Azuma, N.; Suzuki, H. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1739. (c) Matano, Y.; Azuma, N.; Suzuki, H. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2543. (d) Matano, Y.; Yoshimune, M.; Suzuki, H. *Tetrahedron Lett.* **1995**, *36*, 7475. (e) Matano, Y.; Yoshimune, M.; Azuma, N.; Suzuki, H. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1971.

(3) Matano, Y.; Miyamatsu, T.; Suzuki, H. *Chem. Lett.* **1998**, 127. Electron-deficient and sterically crowded aryl ligands such as 4-chlorophenyl, 1-naphthyl, and mesityl groups were not transferred efficiently by this method.

(4) For example, see: (a) Matteson, D. S. In *The Chemistry of the Metal−Carbon Bond*; Hartley, F., Patai, S., Eds.; Wiley: New York, 1987; Vol. 4, p 307. (b) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: New York, 1988. (c) Vaultier, M.; Carboni, B. *Comprehensive Organometallic Chemistry II*; Abel, W. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 11, Chapter 5, p 192.

(5) (a) Matteson, D. S. *Tetrahedron* **1989**, *45*, 1859. (b) Suzuki, A. *Pure Appl. Chem.* **1994**, *66*, 213. (c) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457 and references therein.

(6) Quite recently, Ochiai et al. reported an efficient method for the preparation of vinyl- and aryliodonium salts by the BF_3·OEt_2-promoted reaction between $PhI(OAc)_2$ and vinyl- or arylboronic acids: Ochiai, M.; Toyonari, M.; Nagaoka, T.; Chen, D.-W.; Kida, M. *Tetrahedron Lett.* **1997**, *38*, 6709.

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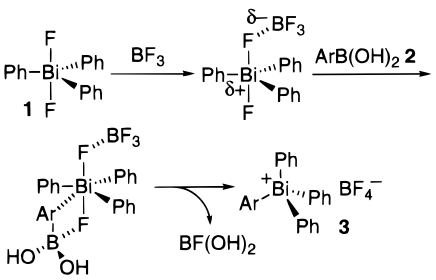
Table 1. Synthesis of Tetraarylbismuthonium Salts[a]

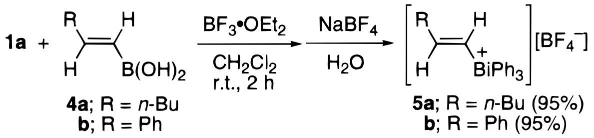
entry no.	**1**	**2**	product (**3**)	yield (%)
1	**1a**	**2a**	$[Ph_4Bi^+][BF_4^-]$ (**3a**)	95
2	**1a**	**2b**	$[Ph_3(4\text{-}MeC_6H_4)Bi^+][BF_4^-]$ (**3b**)	97
3	**1a**	**2c**	$[Ph_3(2\text{-}MeC_6H_4)Bi^+][BF_4^-]$ (**3c**)	97
4	**1a**	**2d**	$[Ph_3(4\text{-}MeOC_6H_4)Bi^+][BF_4^-]$ (**3d**)	96
5	**1a**	**2e**	$[Ph_3(4\text{-}FC_6H_4)Bi^+][BF_4^-]$ (**3e**)	96
6	**1a**	**2f**	$[Ph_3(4\text{-}ClC_6H_4)Bi^+][BF_4^-]$ (**3f**)	97
7	**1a**	**2g**	$[Ph_3(4\text{-}CH_2{=}CHC_6H_4)Bi^+][BF_4^-]$ (**3g**)	95
8[b]	**1a**	**2h**	$[Ph_3(3\text{-}NO_2C_6H_4)Bi^+][BF_4^-]$ (**3h**)	55
9	**1a**	**2i**	$[Ph_3(2,4,6\text{-}Me_3C_6H_2)Bi^+][BF_4^-]$ (**3i**)	98
10	**1a**	**2j**	$[Ph_3(1\text{-}C_{10}H_7)Bi^+][BF_4^-]$ (**3j**)	93
11	**1a**	**2k**	$[Ph_3(2\text{-}C_4H_3S)Bi^+][BF_4^-]$ (**3k**)	98
12	**1a**	**2l**	$[Ph_3(2\text{-}C_4H_3O)Bi^+][BF_4^-]$ (**3l**)	96
13	**1b**	**2a**	$[(4\text{-}MeC_6H_4)_3PhBi^+][BF_4^-]$ (**3m**)	98
14	**1c**	**2a**	$[(4\text{-}MeOC_6H_4)_3PhBi^+][BF_4^-]$ (**3n**)	99
15	**1d**	**2a**	$[(4\text{-}ClC_6H_4)_3PhBi^+][BF_4^-]$ (**3o**)	95

[a] All reagents were used in an equimolar ratio and the reaction was carried out at room temperature for 2 h unless otherwise noted. The yield refers to the isolated yield. [b] Reaction was carried out for 40 h using 4 equiv of $BF_3{\cdot}OEt_2$ and **2h**.

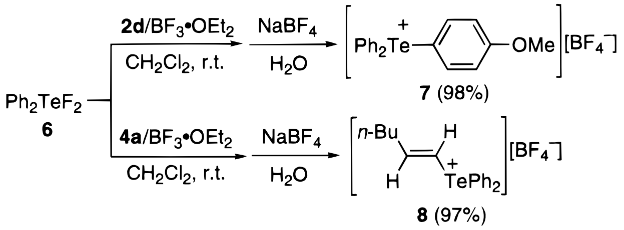
Scheme 2



Scheme 3



Scheme 4



in moderate yield (entry 8). Sterically hindered aryl groups such as mesityl and 1-naphthyl as well as heteroaryl groups such as 2-thienyl and 2-furyl were all smoothly incorporated into the bismuthonium function (entries 9–12). *para*-Substituted derivatives **1b**–**d** were converted to the corresponding bismuthonium salts **3** with similar efficiency (entries 13–15), while tris(2-methylphenyl)bismuth difluoride (**1e**) failed to give the expected bismuthonium salt.

The Bi–C_{aryl} coupling did not take place in the absence of $BF_3{\cdot}OEt_2$, which illustrates the important role of the Lewis acid in this transformation. A plausible reaction pathway is depicted in Scheme 2. A BF_3 molecule coordinates to one of the fluorine atoms in **1** to activate the bismuth center, onto which the aryl group is transferred from **2** via simultaneous ligand exchange in the manner illustrated. No reaction took place between tris(4-methylphenyl)bismuth dichloride and **2a** in the presence of $BF_3{\cdot}OEt_2$ even after 24 h at room temperature. This suggests that the high affinity between the boron and fluorine atoms is an important factor in promoting the Bi–C_{aryl} coupling.

The present method is highly efficient as compared to the previously reported ones for the synthesis of unsymmetrical tetraarylbismuthonium salts[3,9] in that (1) a variety of arylboronic acids are readily available, (2) Bi–C bond formation occurs under mild conditions, and (3) the inorganic products are not toxic. For instance, in our previous method based on arylstannanes, less mild conditions (reflux in CH_2Cl_2, 17–42 h) were needed for the Bi–C_{aryl} coupling and the transferable ligands were limited to tolyl, anisyl, and thioanisyl groups (vide supra).[3]

The reaction also was found to proceed satisfactorily with alkenylboronic acids to give alkenylbismuthonium salts.[2e] Treatment of **1a** with alkenylboronic acids **4** in the presence of $BF_3{\cdot}OEt_2$ afforded the corresponding alkenyltriphenylbismuthonium tetrafluoroborates **5** in good yields (Scheme 3). The stereochemistry of the alkenyl moiety was retained throughout the reaction.

Aryl and alkenylboronic acids could also be employed successfully for the preparation of unsymmetrical telluronium salts. As shown in Scheme 4, (4-methoxyphenyl)- and (1-hexenyl)diphenyltelluronium tetrafluoroborates **7** and **8** were synthesized in excellent yields by the $BF_3{\cdot}OEt_2$-promoted reaction of diphenyltellurinyl difluoride (**6**) with **2d** and **4a**, respectively. Although such telluronium salts have been prepared previously by other methods,[10] the present method affords a simple and reliable route.

The advantage of the boron-based method over the tin-based route[3] is manifested in the synthesis of an asymmetrical bismuthonium salt bearing an oxazoline group *ortho* to the bismuth atom. Thus, the asymmetrically tetraarylated bismuthonium salt **10** was pre-

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(7) A representative procedure is as follows: to a CH_2Cl_2 solution (5 mL) containing triphenylbismuth difluoride (**1a**; 239 mg, 0.50 mmol) and (4-methylphenyl)boronic acid (**2b**; 68 mg, 0.50 mmol) was added $BF_3{\cdot}OEt_2$ (65 μL, 0.50 mmol) at 0 °C, and the mixture was stirred at room temperature for 2 h. An aqueous solution (20 mL) of $NaBF_4$ (500 mg, 4.55 mmol) then was added, and the resulting two-phase mixture was vigorously stirred for 30 min. The water phase was extracted with CH_2Cl_2 (5 mL × 2), and the combined extracts were dried over $MgSO_4$ and passed through a short silica gel column. Evaporation of the solvent under reduced pressure left an oily residue, which was crystallized from Et_2O–CH_2Cl_2 (10:1) to yield (4-methylphenyl)triphenylbismuthonium tetrafluoroborate (**3b**; 300 mg, 97%) as a colorless solid. The NMR monitoring of this reaction using a 0.050 mmol scale of the reagents and 0.5 mL of CD_2Cl_2 revealed that the Bi–C coupling was complete within a few minutes at room temperature.

(8) Inorganic boron compounds were easily removed by washing with water.

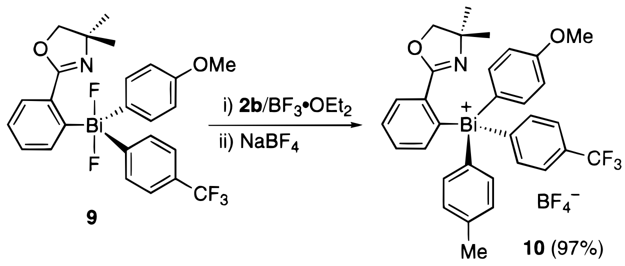
(9) Hellwinkel and Bach prepared unsymmetrical tetraarylbismuthonium salts by the Bi–C bond cleavage of pentaarylbismuth of the type Ph_3BiAr_2 with a protonic or a Lewis acid. Hellwinkel, D.; Bach, M. *Justus Liebigs Ann. Chem.* **1968**, *720*, 198.

(10) For recent syntheses, see: (a) Zhou, Z.-L.; Huang, Y.-Z.; Shi, L.-L.; Hu, J. *J. Org. Chem.* **1992**, *57*, 6598. (b) Xu, C.; Lu, S.; Huang, X. *Synth. Commun.* **1993**, *23*, 2527. (c) Matano, Y.; Suzuki, H.; Azuma, N. *Organometallics* **1996**, *15*, 3760. (d) Shimizu, T.; Urakubo, T.; Kamigata, N. *J. Org. Chem.* **1996**, *61*, 8032.

(11) Compound **9** was prepared from the corresponding triarylbismuthane[12] and XeF_2. See the Supporting Information.

(12) Matano, Y.; Begum, S. A.; Miyamatsu, T.; Suzuki, H. Unpublished results.

Scheme 5



pared in 97% yield from $BF_3{\cdot}OEt_2$, triarylbismuth difluoride **9**,[11] and boronic acid **2b** as depicted in Scheme 5.[13] In contrast, all attempts to obtain the same compound by the BF_3-promoted reaction with tributyl(4-methylphenyl)stannane resulted in the formation of a complex mixture. As expected, the geminal methyl groups in the oxazoline ring were observed as a pair of diastereotopic singlet peaks at δ 0.74 and 0.76 in the ^{1}H NMR spectrum (in $CDCl_3$) of **10** at room temperature, indicating that it has a stable chirality at bismuth on the NMR time scale.[14]

With bismuthonium salt **10** bearing four different aryl ligands in hand, we could investigate the isomerization process at the chiral bismuth center.[15] VT-NMR monitoring of two oxazoline methyl peaks revealed that they were discrete up to 110 °C in pyridine-d_5 and up to 150 °C in 1,2-dichlorobenzene-d_4, suggesting that the chirality of **10** is stable in these temperature ranges. On the basis of these observations, we may conclude that the activation energy ($\Delta G^{\ddagger}$) of the isomerization at the bismuth atom in **10** should be above 23 kcal mol^{-1} in 1,2-dichlorobenzene-d_4 and 21 kcal mol^{-1} in pyridine-d_5, respectively.[16]

The present work provides a new and efficient method for the synthesis of group 15 and 16 *heavy* onium salts based on the combined use of the Lewis acid and boronic acids. Further investigation on the stereochemical behavior of various bismuthonium compounds is now in progress.

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Supporting Information Available: Text giving synthetic, spectroscopic, and analytical data for new compounds (8 pages). Ordering information is given on any current masthead page.

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[13] ^{1}H NMR of **10** ($CDCl_3$): δ 0.74 (s, 3H, oxazoline *Me*), 0.76 (s, 3H, oxazoline *Me*), 2.44 (s, 3H), 3.87 (s, 3H), 4.22 (s, 2H), 7.19 (d, 2H, J = 8.8 Hz), 7.48 (d, 2H, J = 8.0 Hz), 7.60 (d, 2H, J = 8.0 Hz), 7.62−7.67 (m, 3H), 7.78−7.84 (m, 2H), 7.86 (s, 4H), 8.29 (dd, 1H, J = 7.0, 1.5 Hz). Other spectral as well as analytical data are reported in the Supporting Information.

[14] We have previously prepared a bismuthonium salt bearing four different aryl groups as a *d*-camphorsulfonate.[3] However, we could not obtain any positive evidence for the diastereomers; no diastereotopic signals were observed in the ^{1}H NMR spectra, probably due to a weak interaction between the bismuthonium moiety and the counteranion. Therefore, compound **10** is the first example whose chirality is clearly confirmed by a spectroscopic method.

[15] Akiba and co-workers reported the synthesis and VT-NMR study of an asymmetrical hypervalent organobismuth compound (10-Bi-5) bearing a Martin ligand: Chen, X.; Ohdoi, K.; Yamamoto, Y.; Akiba, K. *Organometallics* **1993**, *12*, 1857.

[16] These values were calculated by assuming that the isomerization occurs at 110 °C in pyridine-d_5 and 150 °C in 1,2-dichlorobenzene-d_4.