Synthesis and Reaction of Unsymmetrical Tetraarylbismuthonium Salts. First Isolation of Bismuthonium Salts Bearing All Different Aryl Groups

Yoshihiro Matano,* Takashi Miyamatsu, and Hitomi Suzuki*
Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-01

(Received October 23, 1997; CL-970819)

Successive treatment of triarylbismuth difluorides (**1**) with a Lewis acid, Me_3SiCN, and aryltributylstannanes (**2**) in CH_2Cl_2 gives unsymmetrical tetraarylbismuthonium salts (**3**) in moderate to good yield. The migratory aptitude of an aryl ligand in $[Ph_3ArBi^+][BF_4^-]$ (**3a,b**) in the *C*-arylation of 2-naphthol is Ph>*p*-Tol>*p*-Ans.

Unsymmetrically polyarylated onium compounds, especially chiral ones, have been receiving considerable interest, since their stereochemical behaviors present useful information on the pseudorotation and ligand coupling processes.[1,2] Although a variety of methods are available for the synthesis of this class of compounds derived from the Group 15 elements, little is known for the preparation of bismuth derivatives. The only reported synthesis of unsymmetrical tetraarylbismuthonium compounds involves the Bi–C bond cleavage of pentaarylbismuthoranes as the key step.[3] However, this method does not assure the selective cleavage when two or more analogous aryl ligands are attached to the bismuth center. Herein, we report a new method for the synthesis of unsymmetrical tetraarylbismuthonium salts, based on the Lewis-acid promoted reaction between triarylbismuth difluorides and aryltributylstannanes.[4] This method enabled us to obtain the first bismuthonium salts having the chiral center on the bismuth atom. Some reactions are examined for these new onium compounds.

Successive treatment of triphenylbismuth difluoride (**1a**) with $BF_3{\bullet}OEt_2$, Me_3SiCN, and aryltributylstannanes (**2a-e**) in CH_2Cl_2 gave aryltriphenylbismuthonium tetrafluoroborates (**3a-e**) in 44–85% yields (Scheme 1; Table 1, runs 1–5).[5,6] A typical example is as follows: to a stirred mixture of **1a** (478 mg, 1.00 mmol), $BF_3{\bullet}OEt_2$ (0.13 cm^3, 1.0 mmol), and CH_2Cl_2 (5 cm^3) was added Me_3SiCN (0.13 cm^3, 1.0 mmol) at 0 °C under argon. After 1 h tributyl(2-methoxyphenyl)stannane (**2c**, 398 mg, 1.00 mmol) was added and the resulting mixture was stirred for 24 h under gentle reflux to complete the reaction. Evaporation of the solvent under reduced pressure left an oily residue, which was washed with hexane (5 cm^3 × 3), passed through a short silica-gel column with CH_2Cl_2 as the eluent, and crystallized from Et_2O-CH_2Cl_2 to give 2-methoxyphenyl-(triphenyl)bismuthonium tetrafluoroborate (**3c**, 539 mg, 85.0%) as colorless crystals. When Me_3SiOTf (OTf = OSO_2CF_3) was used in place of $BF_3{\bullet}OEt_2$, the corresponding triflate (**3f**) was obtained (Table 1, run 6). These Lewis acids play dual important roles; they initially enhance the electrophilicity of the bismuth center of **1a** and then are transformed to the corresponding counter anions of **3**. No reaction took place in the absence of such Lewis acids. *p*-Chlorophenyl, α-naphthyl, and *o*-(*N,N*-dimethylaminomethyl)phenyl groups were not efficiently transferred to the bismuth center by the present method.

The methylthio substituent of **3d** can be readily alkylated on the sulfur atom by EtI-$AgBF_4$ to give the corresponding

$$\underset{\mathbf{1a}}{Ph_3BiF_2} + \text{Lewis acid} \xrightarrow[CH_2Cl_2]{Me_3SiCN} \xrightarrow[\text{reflux, 17–42 h}]{n\text{-}Bu_3SnAr\ \mathbf{2}} \underset{\mathbf{3}}{[Ph_3ArBi^+]\,X^-}$$

2,3: **a**, Ar = *p*-MeC_6H_4; **b**, Ar = *p*-$MeOC_6H_4$; **c**, Ar = *o*-$MeOC_6H_4$; **d**, Ar = *p*-$MeSC_6H_4$; **e**, Ar = *o*-$MeSC_6H_4$

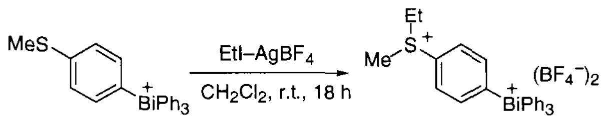
Scheme 1.

Table 1. Arylbismuthonium salts obtained[a]

Run	1	Lewis acid	2	Salt 3	Yield/%
1	**1a**	$BF_3{\bullet}OEt_2$	**2a**	**3a** (X=BF_4)	76
2	**1a**	$BF_3{\bullet}OEt_2$	**2b**	**3b** (X=BF_4)	77
3	**1a**	$BF_3{\bullet}OEt_2$	**2c**	**3c** (X=BF_4)	85
4	**1a**	$BF_3{\bullet}OEt_2$	**2d**	**3d** (X=BF_4)	79
5	**1a**	$BF_3{\bullet}OEt_2$	**2e**	**3e** (X=BF_4)	44
6	**1a**	Me_3SiOTf	**2c**	**3f** (X=OTf)[b]	72
7	**1b**	$BF_3{\bullet}OEt_2$	**2b**	**3h**	71
8	**1c**	$BF_3{\bullet}OEt_2$	**2b**	**3i**	70
9	**1b**	$BF_3{\bullet}OEt_2$	**2d**	**3j**	60

[a] Reagents were used in an equimolar ratio. [b] Ar = *o*-$MeOC_6H_4$.

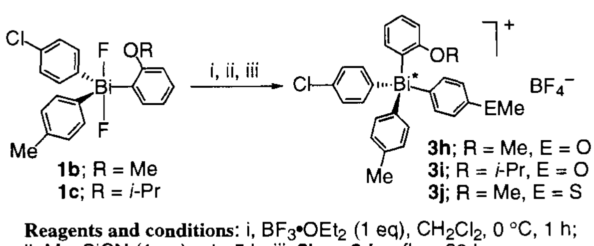
heterobis(onium) salt **3g** (Scheme 2). However, attempted alkylation of **3e** by EtI-$AgBF_4$ failed, showing a lower nucleophilicity of the *ortho*-sulfur atom in **3e**.



3d BF_4^- **3g** (100%)

Scheme 2.

The present methodology finds use in the selective synthesis of bismuthonium salts bearing all different aryl ligands. Thus, the $BF_3{\bullet}OEt_2$-promoted reaction of unsymmetrical triarylbismuth difluorides (**1b,c**) with **2b,d** afforded the corresponding bismuthonium tetrafluoroborates (**3h-j**) bearing all different aryl ligands in 60–71% yields (Scheme 3; Table 1, runs 7-9).[7] This is the first example of the bismuthonium salts having chiral center

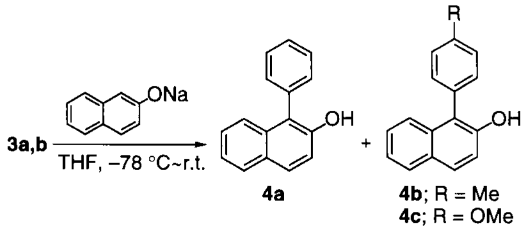


Reagents and conditions: i, $BF_3{\bullet}OEt_2$ (1 eq), CH_2Cl_2, 0 °C, 1 h; ii, Me_3SiCN (1 eq), r.t., 5 h; iii, **2b** or **2d**, reflux, 20 h.

Scheme 3.

on the bismuth atom, *i.e.*, a potential precursor of optically active bismuthonium compounds.[9]

Unsymmetrical bismuthonium salts **3a,b** underwent *C*-arylation with sodium 2-naphtholate, giving 1-aryl-2-naphthols **4** in almost quantitative yields (Scheme 4).[10] The migratory aptitude of the aryl ligands is Ph>p-MeC_6H_4>p-$MeOC_6H_4$, which is the same as that observed in a similar *C*-arylation using p-$Tol_nAr_{3-n}BiCO_3$ (n = 1,2; Ar= p-$NO_2C_6H_4$, p-$MeOC_6H_4$, Ph).[11] As was proposed by Barton and coworkers,[11] the ligand coupling of an intermediary pentavalent species, $Ph_3ArBiOC_{10}H_7$ is most likely to involve the attack of the π-electrons of the enolate moiety on the *ipso*-carbon of the Ar–Bi bond.



Salt	Coupling products (yield)	R/H ratio[a]
3a	**4a** (88%) **4b** (10%)	Me/H (25/75)
3b	**4a** (94%) **4c** (2%)	MeO/H (6/94)

[a] Relative migratory aptitude

Scheme 4.

We acknowledge support of this work by Grants-in-Aid (No. 09239225 and No. 09740469) from the Ministry of Education, Science, Sports and Culture, Japan.

References and Notes

1 For reviews on the chemistry of polyarylated hypervalent heteroatom compounds, see: D. Hellwinkel, *Top. Curr. Chem.*, **109**, 1 (1983); J.-P. Finet, *Chem. Rev.*, **89**, 1487 (1989); G. F. Koser, in "The Chemistry of Functional Groups, Suppl. D," ed by S. Patai and Z. Rappoport, Wiley, Chichester (1983), Chap. 18, p.721; N. Furukawa, in "Heteroatom Chemistry," ed by E. Block, VCH (1990), Chap. 9, p.165; R. Burgada and R. Setton, in "The Chemistry of Organophosphorus Compounds," ed by F. R. Hartley, Wiley, Chichester (1994), Vol. 3, Chap. 3, p. 185; S. Oae, *Pure Appl. Chem.*, **68**, 805 (1996); K.-y. Akiba, *Pure Appl. Chem.*, **68**, 837 (1996), and references cited therein.

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5 All isolated onium compounds **3** gave satisfactory spectral and analytical data. Compound **3c**: mp 130–131 °C; ^{1}H NMR (200 MHz; $CDCl_3$) δ_H 3.86 (s, 3H), 7.28 (t, 1H, J = 8.0 Hz), 7.37 (t, 1H, J = 8.0 Hz), 7.60–7.83 (m, 17H); IR (KBr) ν_{max}/cm^{-1} 1150–950 (BF_4^-); MS (FAB) *m/z* 547 (M^+–BF_4). Anal. Found: C, 47.43; H, 3.48%. Calcd for $C_{25}H_{22}BBiF_4O$: C, 47.34; H, 3.50%. Compound **3h**: glassy solid; ^{1}H NMR (200 MHz; $CDCl_3$) δ_H 2.45 (s, 3H), 3.84 (s, 3H), 3.89 (s, 3H), 7.15–7.85 (m, 16H); IR (KBr) ν_{max}/cm^{-1} 1150–1000 (BF_4^-); MS (FAB) *m/z* 627 (M^+–BF_4, ^{37}Cl), 625 (M^+–BF_4, ^{35}Cl). Anal. Found: C, 45.71; H, 3.60%. Calcd for $C_{27}H_{25}BBiClF_4O_2$: C, 45.50; H, 3.54%.

6 Addition of Me_3SiCN is indispensable for obtainig pure onium salts. NMR study indicated that [Ph_3BiCN][BF_4] was the initially formed species, see: Y, Matano, M. Yoshimune, N. Azuma, and H. Suzuki, *J. Chem. Soc., Perkin Trans. 1*, **1996**, 1971. Stang *et al.* prepared some unsymmetrical iodonium salts using [PhICN][OTf] and organotin reagents, see: B. L. Williamson, R. R. Tykwinski, and P. J. Stang, *J. Am. Chem. Soc.*, **116**, 93 (1994), and references cited therein.

7 Difluorides **1b,c** were prepared by oxidative chlorination of (p-MeC_6H_4)(p-ClC_6H_4)(o-ROC_6H_4)Bi (R = Me,[8] *i*-Pr) with SO_2Cl_2, followed by metathesis of the resulting dichlorides (p-MeC_6H_4)(p-ClC_6H_4)(o-ROC_6H_4)$BiCl_2$ with KF.

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9 Treatment of **3h** (356 mg, 0.499 mmol) absorbed on silica gel with a H_2O solution (30 mL) of sodium *d*-camphorsulfonate (20 equiv) followed by extraction with CH_2Cl_2 gave the corresponding bismuthonium *d*-camphorsulfonate (273 mg, 63.8%), ^{1}H NMR (in $CDCl_3$) spectrum of which showed no diastereotopically separated signals. Addition of europium tris(heptafluorobutanoyl-pivaloylmethanate) did not cause the separation of the signals. At present, it is not clear whether this is due to slight difference in the steric environment around the aryl ligands between two diastereomers or due to the formation of a single diastereomer. Studies on the isolation and isomerization of optically active bismuthonium compounds are now under way.

10 Ph_3Bi and Ph_2(p-RC_6H_4)Bi (R = Me, MeO) were also formed; their yields approximately paralleled with the respective yields of **4b,c** and **4a**.

11 D. H. R. Barton, N. Y. Bhatnagar, J.-P. Finet, and W. B. Motherwell, *Tetrahedron*, **42**, 3111 (1986).