Synthesis and Stereochemical Behavior of Unsymmetrical Tetraarylbismuthonium Salts

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The synthesis and stereochemical behavior of unsymmetrical tetraarylbismuthonium salts were investigated. Two methods (tin and boron methods) for synthesizing unsymmetrically substituted tetraarylbismuthonium salts were developed. In the tin method, successive treatment of triarylbismuth difluorides (**1**; $Ar^1{}_3BiF_2$) with trimethylsilyl cyanide and aryltri-*n*-butylstannanes (**2**; Bu_3SnAr^2) in the presence of a Lewis acid ($BF_3{\cdot}OEt_2$ or Me_3SiOTf) in boiling dichloromethane afforded tetraarylbismuthonium salts (**3**, $[Ar^1{}_3Ar^2Bi^+][BF_4{}^-]$, or **5**, $[Ar^1{}_3Ar^2Bi^+][OTf^-]$) in 44−85% yield. In contrast, in the boron method, similar treatment of **1** with arylboronic acids (**4**; $Ar^2B(OH)_2$) in the presence of $BF_3{\cdot}OEt_2$ afforded the tetrafluoroborates **3** in 55−99% yield at room temperature. Both methods were used to synthesize unsymmetrical tetraarylbismuthonium salts (**9**; $[Ar^1Ar^2Ar^3Ar^4Bi^+][BF_4{}^-]$) starting from unsymmetrical triarylbismuth difluorides **8**. The boron method was also used to synthesize unsymmetrical tetraarylbismuthonium tetrafluoroborates **14** bearing an oxazoline group at the *ortho* position ($[(4\text{-}MeOC_6H_4)(4\text{-}CF_3C_6H_4)(2\text{-}OxC_6H_4)ArBi^+][BF_4{}^-]$; Ox = 4,4-dimethyl-3,4-dihydrooxazol-2-yl; **a**, Ar = 4-MeC_6H_4; **b**, Ar = 2-C_4H_3S). The reaction of bismuthonium tetrafluoroborate **14b** with ammonium tosylate afforded bismuthonium tosylate **15**, which, on treatment with sodium halides, was converted to the corresponding halides **16** ($[(4\text{-}MeOC_6H_4)(4\text{-}CF_3C_6H_4)(2\text{-}OxC_6H_4)(2\text{-}C_4H_3S)Bi^+][X^-]$; **a**, X = Cl; **b**, X = Br; **c**, X = I). Tetrafluoroborates **14** and tosylate **15** are thermally stable, but halides **16** are unstable and underwent ligand coupling in solution. The X-ray diffraction analysis of a tetrafluoroborate **20** ($[(4\text{-}MeC_6H_4)_3(2\text{-}OxC_6H_4)Bi^+][BF_4{}^-]$) revealed a distorted tetrahedral geometry at the bismuth center, which was coordinated by the neighboring oxazoline nitrogen atom. The stereochemical behavior of the synthesized bismuthonium salts was investigated. The signals due to the diastereotopic geminal methyl groups on the oxazoline ring of **14** and **15** did not coalesce in the ^1H NMR spectra in 1,2-dichlorobenzene-d_4 (up to 150 °C), in DMSO-d_6 (up to 135 °C), and in pyridine-d_5 (up to 110 °C), whereas those of chloride **16a** and bromide **16b** coalesced in pyridine-d_5, 1,2-dichlorobenzene-d_4, chlorobenzene-d_5, and toluene-d_8. The coalescence temperature (T_c) depended on the nucleophilicity of the counteranions as well as on the polarity of the solvents; T_c decreased as the nucleophilicity of the counteranions increased or as the polarity of the solvent decreased. Thus, the configuration at bismuth in tetrafluoroborates **14** and tosylate **15** was found to be stable, whereas that in halides **16** strongly depended on the solvent polarity. The observed permutation of bismuthonium halides, $[Ar^1Ar^2Ar^3Ar^4Bi^+][X^-]$, can be explained by a pseudorotation mechanism involving a nonionic pentacoordinate species of the type $Ar^1Ar^2Ar^3Ar^4BiX$.

Introduction

The chirality of a heteroatom center in organic compounds has long been the subject of numerous studies in structural as well as synthetic organic chemistry because it provides valuable information on the stereochemical behavior around the central heteroatom.[3] In the group 15 family, this type of chirality can be constructed by simply attaching different ligands to the heteroatom. Although many organophosphorus and organoarsenic compounds bearing this type of chirality have been studied in detail,[4] the bismuth counterparts have not. Since Bras et al. reported the first example of unsymmetrical bismuthanes in 1981,[5] attention in this area has been focused mainly on organobismuth(III) compounds.[6] Akiba and Yamamoto reported[7] that inversion at the trivalent bismuth center bearing a Martin ligand[8] proceeds via the edge inversion mechanism, which was earlier predicted by Dixon and

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(3) (a) Holms, R. R. *Chem. Rev.* **1990**, *90*, 17. (b) Yamamoto, Y.; Akiba, K.-y. In *Chemistry of Hypervalent Compounds*; Akiba, K.-y., Ed.; Wiley: New York, 1998; Chapter 9, pp 279−294. (c) Kawashima, T. In *Chemistry of Hypervalent Compounds*; Akiba, K.-y., Ed.; Wiley: New York, 1998; Chapter 6, pp 171−210, and references therein.

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Arduengo on the basis of ab initio calculations.[9] Recently, Murafuji et al. successfully isolated the first optically active bismuthane by introducing a chiral iminoferrocenyl group as a coordinating ligand.[10] However, little information is available as yet for unsymmetrical organobismuth(V) compounds that possess chirality at bismuth, and there is a need to determine the factors that affect the permutation process at the bismuth(V) center.[11]

For better understanding of the overall stereochemical behavior around the bismuth(V) center, unsymmetrically substituted tetraarylbismuthonium salts of the type $[Ar^1Ar^2Ar^3Ar^4Bi^+][X^-]$ (X = an anionic species) are considered a good model not only because they would possess reasonable stability for use in kinetic and thermodynamic studies but also because much structural and spectroscopic information is available for compounds of the symmetrical type $[Ar_4Bi^+][X^-]$. Therefore, first a general method must be established for preparation of unsymmetrical bismuthonium salts bearing different aryl ligands, and then the structures and stereochemical behavior of these prepared salts must be determined.[12] Although symmetrical tetraarylbismuthonium salts have been prepared by several methods,[13] compounds of the mixed type $[Ar_3Ar'Bi^+][X^-]$ have only been synthesized by a process that involves the Bi−C bond cleavage of the corresponding pentaarylbismuth ($Ar_3Ar'_2Bi$).[14] This method, however, does not seem to ensure selective Bi−C bond cleavage when four or five similar aryl ligands are attached to the bismuth atom. For the preparation of alkyltriarylbismuthonium salts, we recently reported a general methodology that is based on the Lewis acid-promoted reaction of triarylbismuth difluorides with organosilanes or organostannanes.[15] Due to the certainty in its selective $Bi-C_{alkyl}$ bond formation, in the current study we applied this methodology to the selective $Bi-C_{aryl}$ bond formation to obtain unsymmetrically substituted tetraarylbismuthonium salts.

Here we report the synthesis and stereochemical behavior of tetraarylbismuthonium salts bearing four different aryl ligands.[16] One aim of our current study was to obtain unsymmetrical tetraarylbismuthonium salts that can be used for the direct NMR study on the permutation process. The other aim was to determine the factors that affect the activation energy for the permutation at the bismuth(V) center.

Results

To accomplish our research aims, first we established two methods involving organotin and organoboron reagents, respectively, for the synthesis of tetraarylbismuthonium salts of the type $[Ar_3Ar'Bi^+][X^-]$. These methods then were applied to the preparation of unsymmetrical bismuthonium salts of the type $[Ar^1Ar^2Ar^3Ar^4Bi^+][X^-]$, and finally we investigated, using variable-temperature (VT) NMR spectroscopy, the stereochemical behavior of unsymmetrical tetraarylbismuthonium salts bearing an oxazoline group.

Synthesis of Tetraarylbismuthonium Salts. Compounds of the type $[Ar_3Ar'Bi^+][X^-]$ were prepared as shown in Scheme 1 and Table 1. In the tin method, successive treatment of triphenylbismuth difluoride (**1a**) with trimethylsilyl cyanide (Me_3SiCN) and aryltri-*n*-butylstannanes (**2**) in the presence of a Lewis acid, $BF_3{\cdot}OEt_2$, in CH_2Cl_2 afforded aryltriphenylbismutho-

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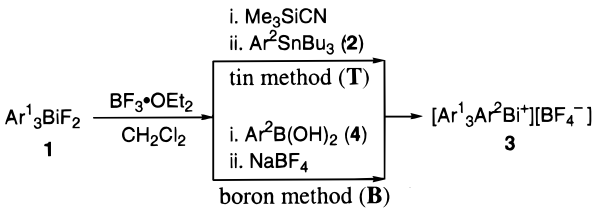
Scheme 1



1a; Ar^1 = Ph
b; Ar^1 = 4-MeC_6H_4
c; Ar^1 = 4-$MeOC_6H_4$
d; Ar^1 = 4-ClC_6H_4
e; Ar^1 = 2-MeC_6H_4

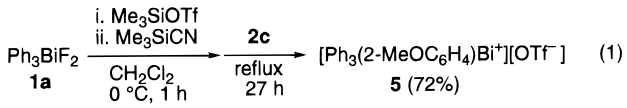
2a; Ar^2 = 4-MeC_6H_4
b; Ar^2 = 4-$MeOC_6H_4$
c; Ar^2 = 2-$MeOC_6H_4$
d; Ar^2 = 2-*i*-$PrOC_6H_4$
e; Ar^2 = 4-$MeSC_6H_4$
f; Ar^2 = 2-$MeSC_6H_4$

4a; Ar^2 = Ph
b; Ar^2 = 4-MeC_6H_4
c; Ar^2 = 2-MeC_6H_4
d; Ar^2 = 4-$MeOC_6H_4$
e; Ar^2 = 4-$MeSC_6H_4$
f; Ar^2 = 4-FC_6H_4
g; Ar^2 = 4-ClC_6H_4
h; Ar^2 = 3-$NO_2C_6H_4$
i; Ar^2 = 4-$MeCOC_6H_4$
j; Ar^2 = 2,4,6-$Me_3C_6H_2$
k; Ar^2 = 1-Naphthyl
l; Ar^2 = 2-Thienyl
m; Ar^2 = 2-Furyl
n; Ar^2 = 4-CH_2=CHC_6H_4

nium tetrafluoroborates (**3**) in 44−85% yield. Because the reaction proceeded very slowly at room temperature, the reaction mixture was heated at gentle reflux for 17−42 h. The boron trifluoride was converted to tetrafluoroborate, and thus the counteranion in **3** came from the Lewis acid. Addition of Me_3SiCN was required to obtain high-purity onium salts.[17] In the absence of Me_3SiCN, tetraphenylbismuthonium tetrafluoroborate was formed as a contaminant. Only electron-rich aryl ligands, such as tolyl, anisyl, and thioanisyl groups, were transferred efficiently by using the tin method. Electron-deficient and sterically hindered aryl ligands, such as 4-chlorophenyl, 1-naphthyl, and mesityl, were not transferred efficiently.

In the boron method, we used arylboronic acids (**4**) because they are more effective as the aryl ligand source.[18,19] Thus, treatment of difluorides **1** with arylboronic acids **4** in the presence of BF_3·OEt_2 in CH_2Cl_2 afforded the corresponding tetraarylbismuthonium tetrafluoroborates **3** within 2 h at room temperature.[20] These were easily isolated by recrystallization from CH_2Cl_2/Et_2O (1:10). By the boron method, a variety of ligands could be connected to the bismuth center in high yield. Aryl ligands bearing an electron-donating or electron-withdrawing substituent were transferable with similar ease and efficiency (entries 7−13). When the reaction was carried out for 24 h with an excess of the reagents, 3-nitrophenyl and 4-acetylphenyl groups also could be transferred in 55−56% yield (entries 14, 15). Sterically hindered aryl groups, such as mesityl and 1-naphthyl, as well as heteroaryl groups, such as 2-thienyl and 2-furyl, were all efficiently transferred to the bismuth atom (entries 16−19). The 4-vinylphenyl group remained intact throughout the reaction (entry 20). Although *para*-substituted triarylbismuth difluorides **1b**−**d** all reacted similarly with **4a**, tris(2-methylphenyl)bismuth difluoride **1e** failed to afford the expected onium salt (entries 21−24). Tris(4-methylphenyl)bismuth *dichloride* and **2a** did not react in the presence of BF_3·OEt_2 even after 24 h at room temperature.

When a different Lewis acid, trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf), was used, the corresponding bismuthonium triflate **5** was obtained (eq 1). No Bi−C_{aryl} coupling occurred in the absence of the given Lewis acid.



(1)

Tetraarylbismuthonium salts **3** and **5** are colorless solids that are thermally stable and readily soluble in CH_2Cl_2, $CHCl_3$, MeCN, and DMSO, but are almost insoluble in toluene and Et_2O. The IR spectra of these salts show strong absorption at around 1150−900 cm^{-1} due to the counteranion (BF_4^- or OTf^-). The FAB mass spectra show a strong fragment peak due to [$Ar^1{}_3Ar^2Bi^+$] ([$M^+ - X$]; X = BF_4, OTf). These data support the onium nature of the bismuth center in **3** and **5**. Tetraphenylbismuthonium salts bearing similar counteranions are known to have an ionic nature.[13]

Synthesis of Unsymmetrical Bismuthonium Salts Bearing Four Different Aryl Ligands. Both the tin and boron methods were used to synthesize bismuthonium salts that bear four different aryl ligands. Unsymmetrical triarylbismuthanes **6**, prepared from mixed diarylbismuth triflate−HMPA complexes and Grignard reagents as reported,[6e] were reacted with sulfuryl chloride to afford triarylbismuth dichlorides **7**. When treated with an excess of potassium fluoride in EtOH/H_2O, dichlorides **7** were converted to the corresponding difluorides **8** in 66−84% yield (Scheme 2).

Successive treatment of **8** with Me_3SiCN and arylstannanes **2** in the presence of BF_3·OEt_2 in boiling CH_2Cl_2 afforded the desired unsymmetrical tetraarylbismuthonium salts **9** in 60−71% yield. When boronic acids **4** were used instead of stannanes **2**, these salts were obtained in better yield (95−97%) within 1 h at room temperature (Scheme 3). The results are summarized in Table 2. Attempts to obtain single crystals of **9** for X-ray analysis failed.

Treatment of **9a** with a large excess of (*d*)-camphor-10-sulfonic acid sodium salt supported on a silica gel afforded the corresponding bismuthonium camphorsulfonate **10** as a pasty solid in 64% yield (eq 2). Despite the presence of two chiral centers, one each at the bismuth and the counteranion, compound **10** showed a single set of peaks in the ^1H NMR spectrum that could not be resolved even by the use of a shift reagent,

(17) A combination of Me_3SiCN and organostannanes was succsessfully employed for the synthesis of iodonium salts, see: Williamson, B. L.; Tykwinski, R. R.; Stang, P. J. *J. Am. Chem. Soc.* **1994**, *116*, 93, and references therein.

(18) Ochiai et al. reported the synthesis of aryl- and alkenyliodonium salts by the Lewis acid-promoted reaction of (diacetoxyiodo)benzene with the corresponding boronic acids: Ochiai, M.; Toyonari, M.; Nagaoka, T.; Chen, D.-W.; Kida, M. *Tetrahedron Lett.* **1997**, *38*, 6709.

(19) Morgan and Pinhey used arylboronic acids for the in situ generation of aryllead triacetates: Morgan, J.; Pinhey, J. T. *J. Chem. Soc., Perkin Trans. 1* **1990**, 715.

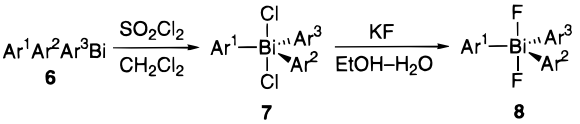
(20) The ^1H NMR monitoring of this reaction using a 0.050 mmol scale of the reagents and 0.5 mL of CD_2Cl_2 revealed that the Bi−C coupling is complete within a few minutes at room temperature.

Table 1. Synthesis of Tetraarylbismuthonium Tetrafluoroborates 3

entry	method[a]	1	2/4	conditions	bismuthonium tetrafluoroborate (3)	yield (%)
1	T	**1a**	**2a**	reflux, 17 h	$[Ph_3(4\text{-}MeC_6H_4)Bi^+][BF_4^-]$ (**3a**)	76
2	T	**1a**	**2b**	reflux, 32 h	$[Ph_3(4\text{-}MeOC_6H_4)Bi^+][BF_4^-]$ (**3b**)	77
3	T	**1a**	**2c**	reflux, 17 h	$[Ph_3(2\text{-}MeOC_6H_4)Bi^+][BF_4^-]$ (**3c**)	85
4	T	**1a**	**2d**	reflux, 24 h	$[Ph_3(2\text{-}i\text{-}PrOC_6H_4)Bi^+][BF_4^-]$ (**3d**)	60
5	T	**1a**	**2e**	reflux, 42 h	$[Ph_3(4\text{-}MeSC_6H_4)Bi^+][BF_4^-]$ (**3e**)	79
6	T	**1a**	**2f**	reflux, 28 h	$[Ph_3(2\text{-}MeSC_6H_4)Bi^+][BF_4^-]$ (**3f**)	44
7	B	**1a**	**4a**	rt, 2 h	$[Ph_4Bi^+][BF_4^-]$ (**3g**)	95
8	B	**1a**	**4b**	rt, 2 h	**3a**	97
9	B	**1a**	**4c**	rt, 2 h	$[Ph_3(2\text{-}MeC_6H_4)Bi^+][BF_4^-]$ (**3h**)	97
10	B	**1a**	**4d**	rt, 2 h	**3b**	96
11	B	**1a**	**4e**	rt, 2 h	**3e**	95
12	B	**1a**	**4f**	rt, 2 h	$[Ph_3(4\text{-}FC_6H_4)Bi^+][BF_4^-]$ (**3i**)	96
13	B	**1a**	**4g**	rt, 2 h	$[Ph_3(4\text{-}ClC_6H_4)Bi^+][BF_4^-]$ (**3j**)	97
14	B	**1a**	**4h**	rt, 24 h	$[Ph_3(3\text{-}NO_2C_6H_4)Bi^+][BF_4^-]$ (**3k**)	55
15	B	**1a**	**4i**	rt, 24 h	$[Ph_3(4\text{-}MeCOC_6H_4)Bi^+][BF_4^-]$ (**3l**)	56
16	B	**1a**	**4j**	rt, 2 h	$[Ph_3(2,4,6\text{-}Me_3C_6H_2)Bi^+][BF_4^-]$ (**3m**)	98
17	B	**1a**	**4k**	rt, 2 h	$[Ph_3(1\text{-}C_{10}H_7)Bi^+][BF_4^-]$ (**3n**)	93
18	B	**1a**	**4l**	rt, 2 h	$[Ph_3(2\text{-}C_4H_3S)Bi^+][BF_4^-]$ (**3o**)	98
19	B	**1a**	**4m**	rt, 2 h	$[Ph_3(2\text{-}C_4H_3O)Bi^+][BF_4^-]$ (**3p**)	96
20	B	**1a**	**4n**	rt, 2 h	$[Ph_3(4\text{-}CH_2{=}CHC_6H_4)Bi^+][BF_4^-]$ (**3q**)	95
21	B	**1b**	**4a**	rt, 2 h	$[(4\text{-}MeC_6H_4)_3PhBi^+][BF_4^-]$ (**3r**)	98
22	B	**1c**	**4a**	rt, 2 h	$[(4\text{-}MeOC_6H_4)_3PhBi^+][BF_4^-]$ (**3s**)	99
23	B	**1d**	**4a**	rt, 2 h	$[(4\text{-}ClC_6H_4)_3PhBi^+][BF_4^-]$ (**3t**)	95
24	B	**1e**	**4a**	rt, 24 h	no Bi−C coupling	

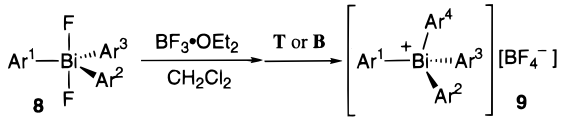
[a] T: (i) $BF_3{\cdot}OEt_2$, 0 °C, 1 h; (ii) Me_3SiCN, 0 °C, 1 h; (iii) **2**, reflux, 17−42 h. B: (i) $BF_3{\cdot}OEt_2$ and **4**, rt, 2−24 h; (ii) $NaBF_4$aq, rt, 20 min.

Scheme 2



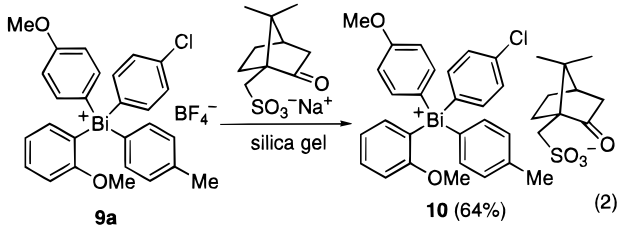
6,7,8a: Ar^1=2-$MeOC_6H_4$, Ar^2=4-ClC_6H_4, Ar^3=4-MeC_6H_4
b: Ar^1=2-MeC_6H_4, Ar^2=4-ClC_6H_4, Ar^3=4-$MeOC_6H_4$
c: Ar^1=2-*i*-$PrOC_6H_4$, Ar^2=4-ClC_6H_4, Ar^3=4-MeC_6H_4

Scheme 3



T; i) Me_3SiCN, 0 °C 1 h; ii) Ar^4SnBu_3, reflux 20 h.
B; i) $Ar^4B(OH)_2$, r.t., 1 h; ii) aq$NaBF_4$, r.t., 20 min.

europium tris(heptafluorobutanoylpivaloylmethanate). Attempts to separate diastereomers by fractional recrystallization also failed due to the poor crystallinity of **10**. At present, we have no direct evidence for the occurrence of chirality at bismuth in camphorsulfonate **10**.



Therefore we next synthesized unsymmetrical bismuthonium salts that bear prochiral substituents in the neighborhood of the bismuth center. In this synthesis, we chose the 2-(4,4-dimethyl-3,4-dihydrooxazol-2-yl)-phenyl group[21] as the aryl ligand, because the two geminal methyl groups on the oxazoline ring were expected to reflect the stability of configuration at bismuth.[22] If the configuration is stable on the NMR time scale, these *gem*-methyl peaks should be diastereotopic in the ^1H NMR spectra.

Scheme 4 illustrates the synthesis of the target compounds **14**. Reaction of tris(4-methoxyphenyl)bismuthane with triflic acid in the presence of HMPA and subsequent treatment with 2-(4,4-dimethyl-3,4-dihydrooxazol-2-yl)phenylmagnesium bromide afforded 2-(4,4-dimethyl-3,4-dihydrooxazol-2-yl)phenylbis(4-methoxyphenyl)bismuthane (**11**) in 73% yield. Selective Bi−C_{anisyl} bond cleavage of **11** with triflic acid and subsequent treatment with an excess of 4-(trifluoromethyl)phenylmagnesium bromide in THF at 0 °C afforded unsymmetrical bismuthane **12** in 60% yield after fractional recrystallization from benzene/MeOH. As expected, the geminal methyl peaks of **12** were diastereotopic, thus indicating that the bismuth center in **12** possesses a stable configuration on the NMR time scale.[23] Oxidative fluorination of **12** with xenon difluoride in MeCN/CH_2Cl_2 afforded the corresponding difluoride **13** as a crystalline solid in 87% yield. The $BF_3{\cdot}OEt_2$-promoted reaction of **13** with arylboronic acids **4b**,**l** afforded tetraarylbismuthonium tetrafluoroborates **14a**,**b** in 97% and 72% yield, respectively. Compound **14a** was a pasty solid, whereas **14b** was a crystalline solid as obtained by recrystallization from CH_2Cl_2/Et_2O. In contrast, the $BF_3{\cdot}OEt_2$-promoted reaction of **13** with Me_3SiCN/arylstannane **2a** afforded a complex mixture after 24 h in boiling CH_2Cl_2.

Treatment of tetrafluoroborate **14b** with a large excess of tetraethylammonium tosylate in CH_2Cl_2 af-

(21) Meyers, A. I.; Temple, D. L.; Haidukewych, D.; Mihelich, E. D. *J. Org. Chem.* **1974**, *39*, 2787.

(22) This type of oxazoline group has been widely used in asymmetric organic synthesis. (a) Peer, M.; deJong, J. C.; Kiefer, M.; Langer, T.; Rieck, H.; Schell, H.; Sennhenn, P.; Sprinz, J.; Steinhagen, H.; Wiese, B.; Helmchen, G. *Tetrahedron* **1996**, *52*, 7547. (b) von Matt, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566. (c) Dawson, G. J.; Frost, C. G.; Williams, J. M. J.; Coote, S. J. *Tetrahedron Lett.* **1993**, *34*, 3149, and references therein.

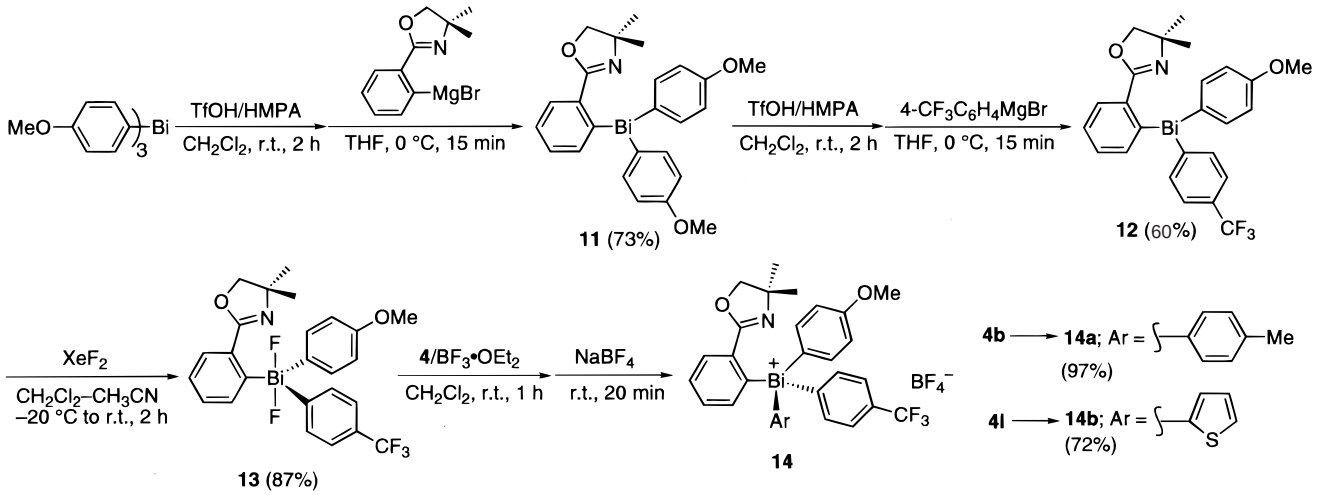
(23) δ 1.11 (s, 3H) and 1.13 (s, 3H) in $CDCl_3$.

Table 2. Synthesis of Tetraarylbismuthonium Tetrafluoroborates 9

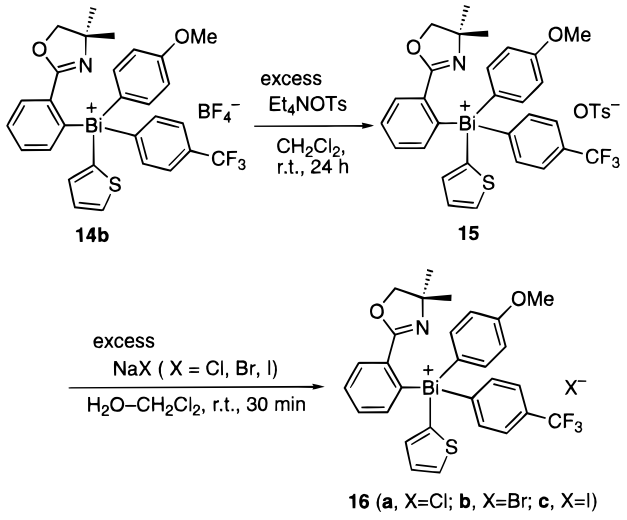
entry	method[a]	8	2/4	$[Ar^1Ar^2Ar^3Ar^4Bi^+][BF_4^-]$ (**9**)	yield (%)
1	T	**8a**	**2b**	$[(2\text{-}MeOC_6H_4)(4\text{-}MeC_6H_4)(4\text{-}ClC_6H_4)(4\text{-}MeOC_6H_4)Bi^+][BF_4^-]$ (**9a**)	71
2	B	**8a**	**4d**	**9a**	97
3	T	**8a**	**2d**	$[(2\text{-}MeOC_6H_4)(4\text{-}MeC_6H_4)(4\text{-}ClC_6H_4)(2\text{-}i\text{-}PrOC_6H_4)Bi^+][BF_4^-]$ (**9b**)	65
4	T	**8a**	**2e**	$[(2\text{-}MeOC_6H_4)(4\text{-}MeC_6H_4)(4\text{-}ClC_6H_4)(4\text{-}MeSC_6H_4)Bi^+][BF_4^-]$ (**9c**)	60
5	B	**8a**	**4e**	**9c**	97
6	B	**8b**	**4l**	$[(4\text{-}MeOC_6H_4)(2\text{-}MeC_6H_4)(4\text{-}ClC_6H_4)(2\text{-}C_4H_3S)Bi^+][BF_4^-]$ (**9d**)	95
7	T	**8c**	**2b**	$[(2\text{-}i\text{-}PrOC_6H_4)(4\text{-}MeC_6H_4)(4\text{-}ClC_6H_4)(4\text{-}MeOC_6H_4)Bi^+][BF_4^-]$ (**9e**)	70

[a] T: (i) $BF_3{\cdot}OEt_2$, 0 °C, 1 h; (ii) Me_3SiCN, 0 °C, 1 h; (iii) **2**, reflux, 20 h. B: (i) $BF_3{\cdot}OEt_2$ and **4**, rt, 1 h; (ii) $NaBF_4$aq, rt, 20 min.

Scheme 4



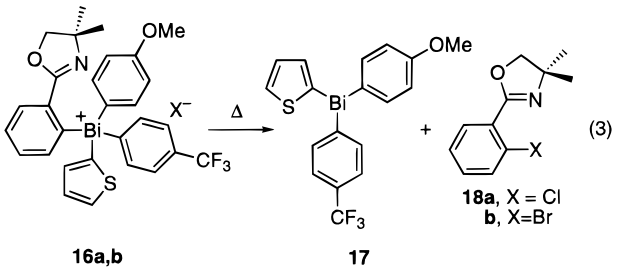
Scheme 5



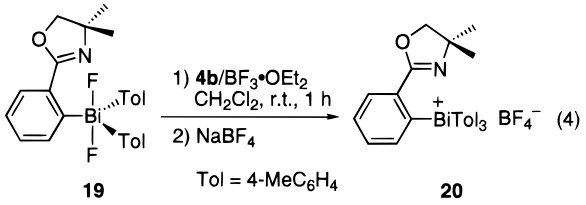
forded the corresponding tosylate **15** in 83% yield. Compound **15** was further converted to chloride **16a**, bromide **16b**, and iodide **16c** by treatment with the respective sodium halides in CH_2Cl_2/H_2O (Scheme 5). Chloride **16a** and bromide **16b** were isolated as powders by recrystallization from CH_2Cl_2/hexane. Iodide **16c** was also obtained as a powder that was approximately 95% pure (based on ^1H NMR).

Unsymmetrical tetraarylbismuthonium salts **14**, **15**, and **16** were characterized using spectroscopic analyses. For all prepared salts, the geminal methyl groups on the oxazoline ring appeared as a pair of diastereotopic singlet peaks in the ^1H NMR spectra at room temperature (in $CDCl_3$). This appearance indicates the stable configuration at bismuth on this NMR time scale.[24]

The halides **16a**,**b** were thermally unstable; when heated in 1,2-dichlorobenzene-d_4 or chlorobenzene-d_5, they decomposed with surprising exclusively to bismuthane **17** and the corresponding haloarene **18a**,**b** (eq 3). In contrast, tetrafluoroborates **14** and tosylate **15** were thermally stable and showed no sign of decomposition up to 150 °C.



Although solid-state structures of **14**, **15**, and **16** could not be determined, the structure of a bismuthonium salt **20**, synthesized from difluoride **19** and boronic acid **4b** according to eq 4, was characterized by X-ray diffraction analysis. Crystal data and collection parameters are given in Table 3. An ORTEP diagram is shown in Figure 1, and selected bond distances and angles are listed in Table 4.



The bismuth center in **20** possesses a significantly distorted tetrahedral geometry with an average C−Bi−C

(24) δ 0.74 (s, 3H), 0.76 (s, 3H) for **14a**; δ 0.77 (s, 3H), 0.84 (s, 3H) for **14b**; δ 0.80 (s, 3H), 0.83 (s, 3H) for **15** in $CDCl_3$.

Table 3. Crystal Data for 20

formula	$C_{32}H_{33}BBiF_4NO{\cdot}CH_2Cl_2$
a (Å)	10.215(2)
b (Å)	18.268(3)
c (Å)	18.667(1)
β (deg)	94.730(10)
V (Å^3)	3471.6(8)
μ(Mo Kα) (cm^{-1})	52.70
space group	$P2_1/c$
Z value	4
D_{calc} (g cm^{-3})	1.585
T (°C)	26.0
no. of reflns collected	8408
no. of unique reflns	7965
R_{int}	0.054
no. of observations ($I > 2.00\sigma(I)$)	3094
no. of variables	389
R	0.045
R_w	0.064
goodness of fit	1.18

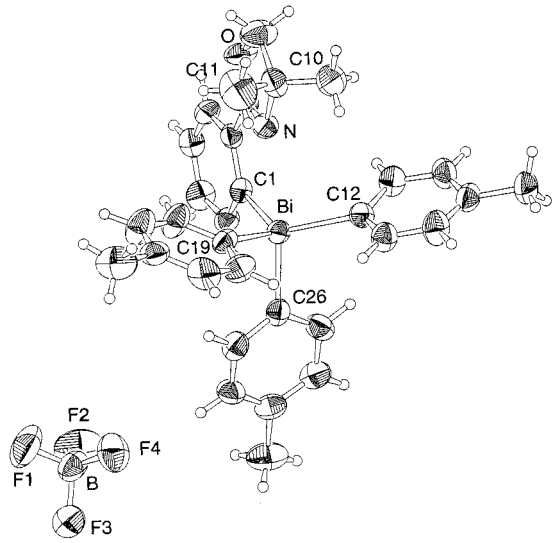


Figure 1. ORTEP drawing of **20** (30% probability ellipsoids) with the atom-numbering scheme. Dichloromethane is omitted for clarity.

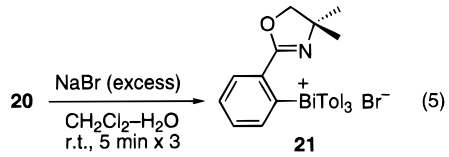
Table 4. Selected Bond Distances (Å) and Angles (deg) for 20

Bi−C(1)	2.21(1)	C(1)−Bi−C(12)	119.2(5)
Bi−C(12)	2.18(1)	C(1)−Bi−C(19)	112.9(4)
Bi−C(19)	2.20(1)	C(1)−Bi−C(26)	98.3(5)
Bi−C(26)	2.21(2)	C(12)−Bi−C(19)	115.5(5)
Bi···N(1)	2.77(1)	C(12)−Bi−C(26)	105.8(5)
		C(19)−Bi−C(26)	101.3(5)

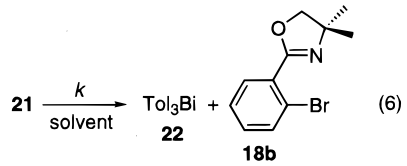
bond angle of 108.8°. The tetrafluoroborate anion is spatially separated from the bismuth cation. The measured Bi−C bond lengths, 2.18(1)−2.21(2) Å, are within the reported range for symmetrical tetraarylbismuthonium compounds.[13b,e,h−j] The oxazoline ring-nitrogen atom is coordinated weakly to the bismuth center with a separation of 2.77 Å, which is longer than the sum of their respective covalent radii (2.16 Å) but much shorter than that of their respective van der Waals radii (ca. 3.6 Å).[25] The oxazoline ring is nearly coplanar with the adjacent benzene ring (dihedral angle is 6.55°), and thus the two geminal methyl groups are located above the neighboring two tolyl rings. These tolyl groups are bent away from the oxazoline moiety, as indicated by the widened C−Bi−C bond angles [112.9(4)−119.2(5)°] between the bismuth and the respective C(1), C(12), and C(19) atoms.

The solid-state structure of **20** seems to be similar to the structure in solution, because the *gem*-methyl groups on the oxazoline ring were observed relatively upfield (δ 0.75 in $CDCl_3$, vs δ 1.41 for **18b**) in the ^{1}H NMR spectrum. This upfield resonance probably is due to the ring-current effect from the neighboring *p*-tolyl groups. Unsymmetrical bismuthonium tetrafluoroborates **14a**,**b** also showed the diastereotopic methyl peaks at δ 0.74−0.84 in $CDCl_3$, suggesting similarity in the structures of **14** and **20**.

Tetrafluoroborate **20** was further converted to the corresponding bromide **21**, a pale yellow solid, by treatment with an excess of sodium bromide (eq 5). Tetrafluoroborate **20** was only slightly soluble in toluene and Et_2O, whereas bromide **21** was soluble. Thus, in the solvents that have lower polarity, the ionic nature of **21** would be considerably less than that of **20**.



Although tetrafluoroborate **20** was stable up to 150 °C in 1,2-dichlorobenzene-d_4, bromide **21** decomposed completely to tris(4-methylphenyl)bismuthane (**22**) and bromoarene **18b** (eq 6). The decomposition rate of **21** in either 1,2-dichlorobenzene-d_4 or toluene-d_8 obeyed first-order kinetics, suggesting that bismuthane **22** and bromoarene **18b** were afforded by the ligand-coupling reaction. The observed rate constants *k* depended on the E_T values[26] of the solvents: 1.6×10^{-3} s^{-1} in 1,2-dichlorobenzene-d_4 (E_T = 38.0) and 2.2×10^{-3} s^{-1} in toluene-d_8 (E_T = 33.9) at 22 °C. Bromide **21** did not decompose over 3 days at 22 °C in DMSO-d_6 (E_T = 45.1). Thus, the decay rate constant increased as the polarity decreased.



Stereochemical Behavior of Unsymmetrical Tetraarylbismuthonium Salts Bearing the Oxazoline Group. The two geminal oxazoline methyl peaks of **14**, **15**, and **16** were used as probes for VT-NMR monitoring of the permutation process around the bismuth center in these onium salts. Halides **16a**,**b** were separately monitored in five organic solvents of different polarity (DMSO-d_6, pyridine-d_5, 1,2-dichlorobenzene-d_4, chlorobenzene-d_5, and toluene-d_8), whereas tetrafluoroborates **14** and tosylate **15** were monitored in the first three of these solvents because they are insoluble in chlorobenzene-d_5 and toluene-d_8. The diastereotopic appearance of the *gem*-methyl peaks of tetrafluorobo-

(25) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. Because the van der Waals radius of bismuth is not yet known, we postulated this value to be similar to that of antimony.

(26) (a) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Liebigs Ann. Chem.* **1963**, *661*, 1. (b) Marcus, Y. *Chem. Soc. Rev.* **1993**, 409.

Table 5. T_c[a] and $\Delta G^{\ddagger}$[b] of 14, 15, and 16a,b

	T_c ($\Delta G^{\ddagger}$)				
salt	DMSO-d_6 [45.1 (29.8)][c]	pyridine-d_5 [40.5 (33.1)][c]	1,2-$Cl_2C_6D_4$ [38.0 (3.0)][c]	ClC_6D_5 [36.8 (3.3)][c]	toluene-d_8 [33.9 (0.1)][c]
14a	>135 (>22.5)	>110 (>20.8)	>150 (>23.0)		
14b	>135 (>21.0)	>110 (>19.2)	>150 (>21.4)		
15		>110 (>20.3)	>150 (>22.5)		
16a	>135 (>21.2)	90 (19.4)	88 (19.4)	85 (19.2)	<25 (−)
16b	>135 (>21.0)	75 (18.9)	73 (18.8)		<25 (−)

[a] Coalescence temperature (°C). [b] Activation energy at T_c (kcal mol^{-1}) estimated from the equation $\Delta G^{\ddagger} = 4.57 \times 10^{-3} T_c[10.32 + \log(T_c \sqrt{2}/\pi\Delta\nu)]$, where $\Delta\nu$ (Hz) is a difference in the resonance between two *gem*-methyl peaks at room temperature. [c] E_T (DN), where E_T is the solvent polarity (see ref 26) and DN is the donor number (see ref 26).

rates **14a**,**b** was discrete up to 135 °C in DMSO-d_6, 110 °C in pyridine-d_5, and 150 °C in 1,2-dichlorobenzene-d_4, although the difference in frequencies ($\delta\nu$) between the two peaks narrowed at high temperatures. These results show that the configuration at the bismuth center in **14** is stable within the temperature ranges considered here.[27] Similarly, the diastereotopic appearance of the *gem*-methyl groups of tosylate **15** was discrete up to 110 °C in pyridine-d_5 and 150 °C in 1,2-dichlorobenzene-d_4. Therefore, we estimated the threshold values for the activation free energy ($\Delta G^{\ddagger}$) of the permutation process in **14** and **15** by assuming that the oxazoline methyl peaks had coalesced at the highest observable temperature in each solvent (Table 5).[28]

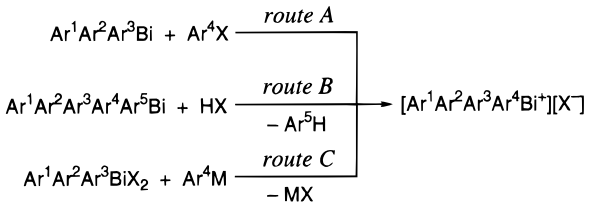
The geminal oxazoline methyl peaks of halides **16a**,**b** coalesced in pyridine-d_5, 1,2-dichlorobenzene-d_4, chlorobenzene-d_5, and toluene-d_8 at the temperature shown in Table 5, but did not coalesce in DMSO-d_6 up to 135 °C. The coalescence temperature (T_c) decreased with decreasing E_T of the solvents in the following order; pyridine-d_5 > 1,2-dichlorobenzene-d_4 > chlorobenzene-d_5. In toluene-d_8, the *gem*-methyl groups appeared as a single broad peak, even at room temperature. The T_c was independent of the concentration of **16a**,**b** in the range 0.008−0.035 M, suggesting that the observed coalescence reflected the intramolecular ligand permutation process. For all solvents, bromide **16b** coalesced at lower temperatures than did chloride **16a**. At temperatures near T_c, halides **16a**,**b** also underwent ligand coupling, thus producing haloarenes **18a**,**b** and bismuthane **17**. The thermal stability of **16** depended on the solvent polarity; for a given temperature, the lifetime of **16a** in decreasing order was pyridine-d_5 > 1,2-dichlorobenzene-d_4 > chlorobenzene-d_5 > toluene-d_8. Thus, the stability of halides **16** increased as the solvent polarity increased.

An equimolar pyridine-d_5 solution of tetraethylammonium bromide and either tetrafluoroborate **14** or tosylate **15** showed coalescence of the *gem*-methyl peaks at around 80 °C, thus leading to gradual formation of bismuthane **17** and bromoarene **18b**. This formation indicated the facile conversion of **14** and **15** to bromide **16b**.

Discussion

Synthesis of Unsymmetrical Tetraarylbismuthonium Salts. There are three possible routes to obtain bismuthonium salts that bear four different aryl ligands (Scheme 6): oxidative arylation of a triarylbismuthane (route A), Bi−C bond cleavage of a pentaarylbismuth (route B), and Bi−C bond construction from a triarylbismuth(V) dihalide and an arylmetal reagent (route C).

Scheme 6



Route A may not be generally applicable because a pair of unshared electrons in triarylbismuthane has low nucleophilicity.[12,15b] For instance, the reaction of tris(4-methylphenyl)bismuthane and 4-nitorophenyldiazonium tetrafluoroborate affords a mixture of triarylbismuthanes [$(4\text{-}MeC_6H_4)_n(4\text{-}NO_2C_6H_4)_{3-n}Bi$; $n = 1$ and 2] instead of the onium salt.[29] The late transition metal-catalyzed arylation, which works well for the preparation of arylphosphonium salts,[30] is unlikely to occur because the Bi−C bonds of bismuthanes are readily cleaved by these transition metal complexes.[31] As mentioned in the Introduction, route B was effective for the synthesis of mixed compounds of the type $[Ar_3Ar'Bi^+][X^-]$.[14] However, this methodology does not seem to ensure the selective cleavage of the Bi−C bond when similar aryl ligands are attached to the bismuth atom. Our results demonstrate that route C is the most general and most reliable for preparing bismuthonium salts that bear four different aryl ligands, because this route is free from the uncertainties involved in routes A and B. In route C, however, a suitable arylating agent must be chosen. Early attempts by Challenger to prepare tetraphenylbismuthonium halides from triphenylbismuth dihalides and phenyl Grignard reagents resulted in the formation of a mixture of phenylbismuthanes Ph_nBiX_{3-n} (n = 1, 2, 3; X = halide) and halobenzene.[32] The Grignard reagents apparently are too reactive to control selective Bi−C bond formation. In contrast, both arylstannanes **2** and arylboronic acids

(27) Because the upper limit of the variable-temperature unit was 150 °C, we did not monitor the NMR peaks above 150 °C.

(28) The $\Delta G^{\ddagger}$ threshold values were estimated by assuming that the methyl peaks had coalesced at 135 °C in DMSO-d_6, 110 °C in pyridine-d_5, and 150 °C in 1,2-dichlorobenzene-d_4. See Experimental Section.

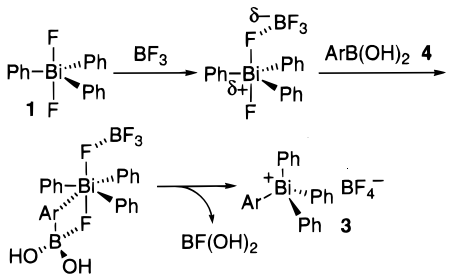
(29) Barton, D. H. R.; Bhatnagar, N. Y.; Finet, J.-P.; Motherwell, W. B. *Tetrahedron* **1986**, *42*, 3111.

(30) (a) Cassar, L.; Fao, M. *J. Organomet. Chem.* **1974**, *74*, 75. (b) Horner, L.; Mummenthey, G.; Moser, H.; Beck, P. *Chem. Ber.* **1966**, *99*, 2782.

(31) For example, see: (a) Barton, D. H. R.; Ozbalik, N.; Ramesh, M. *Tetrahedron* **1988**, *44*, 5661. (b) Cho, C. S.; Yoshimori, Y.; Uemura, S. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 950, and references therein.

(32) (a) Challenger, F. *J. Chem. Soc.* **1914**, *105*, 2210. (b) Challenger, F.; Goddard, A. E. *J. Chem. Soc.* **1920**, *117*, 762.

Scheme 7



4 are milder nucleophilic reagents that can interact with difluorides **1**, but only in the presence of a Lewis acid. A plausible pathway for the boron method is depicted in Scheme 7. A BF_3 molecule coordinates to a fluorine atom in **1** to enhance the electrophilicity of the bismuth center, and the aryl group is transferred from the boron to the bismuth center via simultaneous ligand exchange with fluorine.

Evidence that the high affinity of boron toward fluorine is the key in promoting the $Bi-C_{aryl}$ bond formation is that no reaction occurs when tris(4-methylphenyl)bismuth dichloride is used instead of difluorides **1**.[33] An additional feature of the present tin and boron methods is that tetrafluoroborate and triflate anions are formed directly from the respective Lewis acids used. These weakly coordinating anions guarantee the thermal stability of the resulting bismuthonium salts (see the following section).

On the basis of our results, the boron method has four advantages over the tin method: (a) a variety of arylboronic acids are readily available,[34] (b) Bi−C bond formation occurs under mild conditions, (c) a wide range of aryl ligands are transferable, and (d) inorganic wastes are not toxic. The advantages of the boron method over the tin method are well demonstrated in the synthesis of unsymmetrical bismuthonium salts **14** bearing the oxazoline group *ortho* to the bismuth atom, where the latter method failed to afford the desired product **14**.

Stereochemical Behavior around the Bismuth Center. Our results on the VT-NMR monitoring revealed that both the nucleophilicity of counteranions and the polarity of solvents strongly affect the stereochemical behavior around the bismuth center. Although accurate $\Delta G^{\ddagger}$ values could not be obtained for **14** and **15**, we can qualitatively discuss these two factors based on our results and previous results in the literature. The diastereotopic appearance of the geminal methyl peaks of tetrafluoroborates **14** and tosylate **15** revealed that the ligand permutation in these compounds proceeds very slowly on the NMR time scale. We could not differentiate **14** from **15** in this respect. Conversion of the counteranions to halides, however, brought a dramatic change in the stereochemical stability of bismuthonium salts. The observed findings suggest the acceleration of permutation is due to counteranions that have higher nucleophilicity toward the cationic bismuth center.

The thermal stability of bismuthonium salts in solution also depends on the nucleophilicity of the counteranions involved. The observed instability and the decomposition mode of **16** agree with the general trends reported for tetraphenylbismuthonium halides, i.e., rapid decomposition to halobenzene and triphenylbismuthane via the ligand coupling.[13a] The instability of a Bi(V) compound has recently been confirmed by theoretical analysis.[35] The exclusive formation of bismuthanes **17** and **22** from the respective bromides **16** and **21** indicates that the electropositive *ipso* carbon atom of the oxazoline-substituted phenyl group is much more reactive than other *ipso* carbons.

The stereochemical behavior of unsymmetrical tetraarylbismuthonium salts seems closely related to the coordination geometry at bismuth. Barton et al.[13e] and also Doak and Freedman[13b] observed that tetraphenylbismuth(V) compounds of the type Ph_4BiZ can change the central geometry depending on the coordinating ability of an anionic group Z. Both studies showed that weakly coordinating counteranions favor the tetracoordinate (tetrahedral) onium-type geometry, whereas strongly coordinating anions favor the pentacoordinate (trigonal bipyramidal) structure. Beaumont and Goel investigated the physical properties of several tetraphenylbismuth(V) compounds by IR and Raman spectroscopies and molecular weight and conductance measurements.[13d] They found that a tetrafluoroborate behaves as a 1:1 electrolyte in acetonitrile and nitomethane, whereas a trichloroacetate is nonionic. The observations from these three studies clearly show that counteranions that have higher nucleophilicity are prone to bond tightly with the cationic bismuth atom (either in the solid state or in solution) to favor the pentacoodinate geometry over the ionic tetrahedral structure. Thus, for halides **16**, the bismuth center would readily reorganize its geometry to the nonionic pentacoordinate geometry at high temperatures, whereas in tetrafluoroborates **14** it would maintain the original tetrahedral geometry up to high temperatures.

Honer and Hofer reported that optically active arsonium halides racemize with decreasing ease in the order iodide > bromide > chloride, but those salts containing counteranions that have lower nucleophilicity apparently are stable.[36] These results can be explained by a mechanism involving Berry pseudorotation[37] of a transient pentacoordinate halogenoarsenic(V) intermediate.[4c] Our observed counteranion effect may also be explained in similar terms; the higher the nucleophilicity of a halide, the faster the permutation. A plausible mechanism for the permutation and ligand coupling of halides **16** is depicted in Scheme 8.

At high temperatures, the halide anion moves closer to the cationic bismuth center to generate a pentacoordinate species **A** or **A′** as a transient intermediate. This intermediate then undergoes either several pseudoro-

(33) The B−F bond energy in BF_3 is 646 kJ mol^{-1}, see: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 172, Table 6-2.

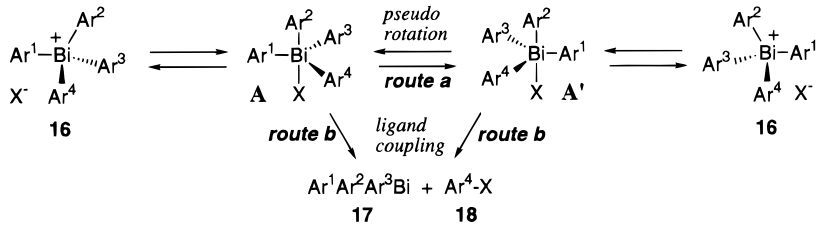
(34) (a) Matteson, D. S. *Tetrahedron* **1989**, *45*, 1859. (b) Suzuki, A. *Pure Appl. Chem*. **1994**, *66*, 213. (c) Miyaura, N.; Suzuki, A. *Chem. Rev*. **1995**, *95*, 2457, and references therein.

(35) Moc, J.; Morokuma, K. *J. Am. Chem. Soc.* **1995**, *117*, 11790. BiH_5 (D_{3h}) is thermodynamically unstable with respect to $BiH_3 + H_2$ by over 70 kcal mol^{-1}. A zwitterionic transition state with axial$^{(-)}$−equatorial$^{(+)}$ polarization is proposed for this ligand-coupling process.

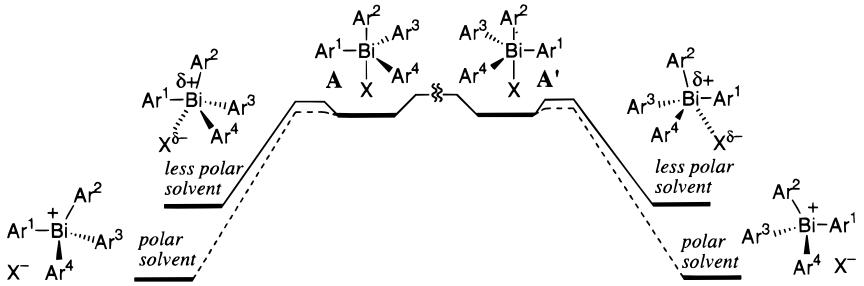
(36) Horner, L.; Hofer, W. *Tetrahedron Lett*. **1965**, 3281.

(37) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

Scheme 8



Scheme 9



tations (*route a*) or reductive coupling (*route b*).[38] The transition-state structures in these stereochemical processes should be similar to the intermediate **A** (**A′**) and would be less polarized compared with the ground-state structure. Recently, Moc and Morokuma carried out ab initio calculations on the stereochemical processes of a series of MH_5 compounds (M = P, As, Sb, Bi) and estimated an energy barrier of the Berry pseudorotation of BiH_5 to be ca. 2 kcal mol^{-1}.[35] This value implies that the interconversion between **A** and **A′** proceeds smoothly with a small activation energy. Therefore, the $\Delta G^{\ddagger}$ values that we estimated in this study may represent the energy necessary to reorganize the coordination geometry of the bismuth from tetracoordinate to pentacoordinate. The relationship between the T_c and the solvent polarity (E_T) also supports this interpretation. The activation energy for the permutation of **16** increases as the polarity of solvents is increased, probably because the ground state of **16** is polarized and becomes stabilized more efficiently relative to the transition state in polar solvents (Scheme 9).

The observed solvent-polarity effect significantly differs from the effect involved in the edge inversion process of unsymmetrical bismuthanes, where nucleophilic solvents such as pyridine and DMSO dramatically stabilize the transition state by coordinating to the trivalent bismuth center.[7] For the bismuth(V) systems that we studied, the donor ability of solvents seems to be less important than the polarity. In fact, no coalescence was observed in DMSO-d_6 for any bismuthonium salt **14**, **15**, and **16**.

Conclusions

The Lewis acid-promoted reaction of triarylbismuth difluorides with arylstannanes or arylboronic acids provides convenient routes to afford unsymmetrically substituted tetraarylbismuthonium salts. The ^{1}H NMR spectra of unsymmetrical tetraarylbismuthonium salts bearing the oxazoline group at the *ortho*-position clearly show the stability of the configuration at bismuth in solution. The stereochemical as well as thermal stability of this class of compounds strongly depends on the nucleophilicity of the counteranions as well as on the polarity of the solvents. Tetrafluoroborates and tosylate salts possess stable configuration, whereas halide salts do not. The permutation of bismuthonium halides, $[Ar^1Ar^2Ar^3Ar^4Bi^+][X^-]$, probably occurs via the ligand reorganization at the bismuth(V) center involving pseudorotations of a nonionic pentacoordinate species of the type $Ar^1Ar^2Ar^3Ar^4BiX$.

Experimental Section

General Procedures. All reactions with air-sensitive compounds were carried out under an atmosphere of argon. All melting points were determined on a Yanagimoto hot-stage apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 or a JEOL FX400 spectrometer using $CDCl_3$ as the solvent unless otherwise noted. Chemical shifts are reported as the relative value versus tetramethylsilane, and coupling constants *J* are given in Hz. Variable-temperature NMR measurements were carried out using a JEOL FX400 spectrometer equipped with a temperature control unit. IR spectra were observed as KBr pellets on a Shimadzu FTIR-8100S spectrophotometer (see Supporting Information for full data of IR spectra). FAB mass spectra were obtained on a JEOL JMS-HS110 spectrometer using 3-nitrobenzyl alcohol as a matrix. Elemental analyses were performed at the Microanalytical Laboratory of Kyoto University. Column chromatography was performed on silica gel (Wakogel C200). Dichloromethane (CH_2Cl_2) was distilled from CaH_2 under argon before use. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl under argon before use.

Materials. Triarylbismuth difluorides **1a**,**b** were prepared according to reported procedures.[39,15b] Difluorides **1c**−**e** were obtained quantitatively from triarylbismuthanes and XeF_2 in CH_2Cl_2 at 0 °C. Aryltributylstannanes **2** were synthesized from chlorotri-*n*-butylstannane and the corresponding aryllithium or aryl Grignard reagents.[40] Arylboronic acids **4a**,**c**,**h**,**i**,**n** were

(38) If the species **A** and **A′** possess trigonal bipyramidal structure with the numbering scheme as illustrated in Scheme 8, the interconversion between **A** and **A′** should involve more than two pseudorotation processes. We believe that the activation energies for all the processes between **A** and **A′** are very small. See ref 3b.

(39) Challenger, F.; Wilkinson, J. F. *J. Chem. Soc.* **1922**, *121*, 91.
(40) Wardell, J. L.; Ahmed, S. *J. Organomet. Chem.* **1974**, *78*, 395.

purchased from Aldrich. Other arylboronic acids were prepared from $B(OR)_3$ (R = Me, *i*-Pr) and the corresponding aryllithium or aryl Grignard reagents according to reported procedures.[19,41] Other reagents were used as commercially received.

Tris(4-methoxyphenyl)bismuth difluoride (1c): pasty solid; ^{1}H NMR (200 MHz) δ 3.82 (s, 9H), 7.14 (d, 6H, J = 8.6), 8.12 (d, 6H, J = 8.6); FABMS m/z 549 ($M^+ - F$).

Tris(4-chlorophenyl)bismuth difluoride (1d): pasty solid; ^{1}H NMR (200 MHz) δ 7.64 (d, 6H, J = 8.7), 8.16 (d, 6H, J = 8.7); FABMS m/z 561 ($M^+ - F$; ^{35}Cl × 3).

Compounds **1c**,**d** were used for the synthesis of **3s**,**t** without further purification.

Tris(2-methylphenyl)bismuth difluoride (1e): mp 165−166 °C (decomp); ^{1}H NMR (200 MHz) δ 2.65 (s, 9H), 7.4−7.55 (m, 9H), 7.82 (m, 3H); FABMS m/z 501 ($M^+ - F$). Anal. Calcd for $C_{21}H_{21}BiF_2$: C, 48.47; H, 4.07. Found: C, 48.36; H, 4.04.

Synthesis of Tetraarylbismuthonium Tetrafluoroborates 3. From Arylstannanes 2 (Tin Method). General Procedure. To a stirred CH_2Cl_2 solution (5 mL) containing triphenylbismuth difluoride **1a** (478 mg, 1.0 mmol) and BF_3·OEt_2 (0.13 mL, 1.0 mmol) was added Me_3SiCN (0.13 mL, 1.0 mmol) at 0 °C. After 1 h, aryltri-*n*-butylstannane **2** (1.0 mmol) was added, and the resulting mixture was heated under gentle reflux for 17−42 h to complete the reaction. Evaporation of the solvent under reduced pressure left an oily residue, which was washed with hexane (5 mL × 3), purified by passing through a short silica gel column with CH_2Cl_2 as the eluent, and crystallized from Et_2O/CH_2Cl_2 (10:1) to give aryltriphenylbismuthonium tetrafluoroborate **3** as a solid. When Me_3SiOTf (0.19 mL, 1.0 mmol) was used instead of BF_3·OEt_2, the bismuthonium triflate **5** was obtained.

From Arylboronic Acids 4 (Boron Method). General Procedure. To a CH_2Cl_2 solution (5 mL) containing triarylbismuth difluoride **1** (0.50 mmol) and arylboronic acid **4** (0.50 mmol) was added BF_3·OEt_2 (65 μL, 0.50 mmol) at 0 °C. The mixture was stirred for 2 h at room temperature. An aqueous solution (20 mL) of $NaBF_4$ (500 mg, 4.55 mmol) was then added, and the resulting two-phase solution was vigorously stirred for a further 20 min. The aqueous phase was separated and extracted with CH_2Cl_2 (5 mL × 2). The combined organic extracts were dried over $MgSO_4$ and passed through a short silica gel column. The eluted solution was evaporated under reduced pressure to leave an oily residue, which was crystallized from Et_2O/CH_2Cl_2 (10:1) to give compound **3** as a crystalline or glassy solid.

(4-Methylphenyl)triphenylbismuthonium tetrafluoroborate (3a): mp 138−139 °C; ^{1}H NMR (200 MHz) δ 2.44 (s, 3H), 7.49 (d, 2H, J = 8.0), 7.57−7.83 (m, 17H); IR ν_{max} 1150−950 (BF_4^-) cm^{-1}; FABMS m/z 531 ($M^+ - BF_4$), 377, 363, 300, 286, 209. Anal. Calcd for $C_{25}H_{22}BBiF_4$: C, 48.57; H, 3.59. Found: C, 48.70; H, 3.61.

(4-Methoxyphenyl)triphenylbismuthonium tetrafluoroborate (3b): glassy solid; ^{1}H NMR (200 MHz) δ 3.86 (s, 3H), 7.20 (d, 2H, J = 8.7), 7.58−7.82 (m, 17H); IR ν_{max} 1150−900 (BF_4^-) cm^{-1}; FABMS m/z 547 ($M^+ - BF_4$), 393, 363, 316, 286, 209. Anal. Calcd for $C_{25}H_{22}BBiF_4O$: C, 47.34; H, 3.50. Found: C, 47.23; H, 3.48.

(2-Methoxyphenyl)triphenylbismuthonium tetrafluoroborate (3c): mp 130−131 °C; ^{1}H NMR (200 MHz) δ 3.86 (s, 3H), 7.28 (t, 1H, J = 8.0), 7.37 (d, 1H, J = 8.0), 7.60−7.83 (m, 17H); IR ν_{max} 1150−900 (BF_4^-) cm^{-1}; FABMS m/z 547 ($M^+ - BF_4$), 393, 363, 316, 286, 209. Anal. Calcd for $C_{25}H_{22}BBiF_4O$: C, 47.34; H, 3.50. Found: C, 47.43; H, 3.48.

(2-Isopropoxyphenyl)triphenylbismuthonium tetrafluoroborate (3d): mp 170−172 °C; ^{1}H NMR (200 MHz) δ 0.99 (d, 6H, J = 6.0), 4.71 (sept, 1H, J = 6.0), 7.20−7.35 (m, 2H), 7.55−7.90 (m, 17H); IR ν_{max} 1150−950 (BF_4^-) cm^{-1}; FABMS m/z 575 ($M^+ - BF_4$), 421, 363, 344, 286, 209. Anal. Calcd for $C_{27}H_{26}BBiF_4O$: C, 48.97; H, 3.96. Found: C, 48.74; H, 3.96.

(4-Methylthiophenyl)triphenylbismuthonium tetrafluoroborate (3e): mp 141−143 °C; ^{1}H NMR (200 MHz) δ 2.49 (s, 3H), 7.46 (d, 2H, J = 8.6), 7.55−7.82 (m, 17H); IR ν_{max} 1150−900 (BF_4^-) cm^{-1}; FABMS m/z 563 ($M^+ - BF_4$), 409, 363, 332, 286, 209. Anal. Calcd for $C_{25}H_{22}BBiF_4S$: C, 46.17; H, 3.41. Found: C, 45.93; H, 3.49.

(2-Methylthiophenyl)triphenylbismuthonium tetrafluoroborate (3f): glassy solid; ^{1}H NMR (200 MHz) δ 2.27 (s, 3H), 7.55−7.90 (m, 19H); FABMS m/z 563 ($M^+ - BF_4$), 409, 363, 332, 286, 209. This compound was further transformed into hexafluorophosphate by treatment with aqueous ammonium hexafluorophosphate: mp 207−209 °C; ^{1}H NMR (200 MHz) δ 2.30 (s, 3H), 7.60−7.92 (m, 19H); IR ν_{max} 900−800 (PF_6^-) cm^{-1}; FABMS m/z 563 ($M^+ - PF_6$), 409, 363, 332, 286, 209. Anal. Calcd for $C_{25}H_{22}BBiF_6PS$: C, 42.38; H, 3.13. Found: C, 42.55; H, 3.09.

Tetraphenylbismuthonium tetrafluoroborate (3g): mp 243−244 °C (lit.,[42] 236 °C); ^{1}H NMR (200 MHz) δ 7.5−7.8 (m, 20H); ^{13}C NMR (50 MHz) δ 132.5, 132.6, 135.1, 137.3; FABMS m/z 517 ($M^+ - BF_4$).

(2-Methylphenyl)triphenylbismuthonium tetrafluoroborate (3h): mp 197−198 °C; ^{1}H NMR (200 MHz) δ 2.44 (s, 3H), 7.40−7.90 (m, 19H); IR ν_{max} 1150−950 (BF_4^-) cm^{-1}; FABMS m/z 531 ($M^+ - BF_4$), 377, 363, 300, 286, 209. Anal. Calcd for $C_{25}H_{22}BBiF_4$: C, 48.57; H, 3.59. Found: C, 48.55; H, 3.48.

(4-Fluorophenyl)triphenylbismuthonium tetrafluoroborate (3i): mp 172−173 °C; ^{1}H NMR (400 MHz) δ 7.36 (t, 2H, J = 8.4), 7.62 (t, 3H, J = 7.2), 7.68 (t, 6H, J = 7.4), 7.79 (d, 6H, J = 7.6), 7.84 (dd, 2H, J = 8.4, 5.5); IR ν_{max} 1150−950 (BF_4^-) cm^{-1}; FABMS m/z 535 ($M^+ - BF_4$), 209. Anal. Calcd for $C_{24}H_{19}BBiF_5$: C, 46.33; H, 3.08. Found: C, 46.36; H, 3.02.

(4-Chlorophenyl)triphenylbismuthonium tetrafluoroborate (3j): mp 123−124 °C; ^{1}H NMR (200 MHz) δ 7.56−7.86 (m, 19H); IR ν_{max} 1150−900 (BF_4^-) cm^{-1}; FABMS m/z 551 ($M^+ - BF_4$; ^{35}Cl), 363, 286, 209. Anal. Calcd for $C_{24}H_{19}BBiClF_4$: C, 45.14; H, 3.00. Found: C, 45.39; H, 2.98.

(3-Nitrophenyl)triphenylbismuthonium tetrafluoroborate (3k): mp 218−220 °C; ^{1}H NMR (200 MHz) δ 7.64 (t, 3H, J = 7.3), 7.69 (t, 6H, J = 7.3), 7.81 (d, 6H, J = 7.4), 7.86 (t, 1H, J = 7.8), 8.29 (d, 1H, J = 7.5), 8.41 (d, 1H, J = 7.9), 8.50 (s, 1H); IR ν_{max} 1524 (NO_2), 1345 (NO_2), 1200−950 (BF_4^-) cm^{-1}; FABMS m/z 562 ($M^+ - BF_4$), 546, 408, 363, 286, 209. Anal. Calcd for $C_{24}H_{19}BBiF_4NO_2$: C, 44.40; H, 2.95; N, 2.16. Found: C, 44.92; H, 2.90; N, 2.40.

(4-Acetylphenyl)triphenylbismuthonium tetrafluoroborate (3l): mp 166−168 °C; ^{1}H NMR (200 MHz) δ 2.64 (s, 3H), 7.60−7.88 (m, 15H), 7.95 (d, 2H, J = 8.3), 8.20 (d, 2H, J = 8.3); IR ν_{max} 1686 (C=O), 1150−950 (BF_4^-) cm^{-1}; FABMS m/z 559 ($M^+ - BF_4$), 405, 363, 328, 286, 209. Anal. Calcd for $C_{26}H_{22}BBiF_4O$: C, 48.32; H, 3.43. Found: C, 48.27; H, 3.37.

Mesityltriphenylbismuthonium tetrafluoroborate (3m): mp 219−220 °C; ^{1}H NMR (200 MHz) δ 2.33 (s, 6H), 2.36 (s, 3H), 7.17 (s, 2H), 7.52−7.70 (m, 9H), 7.80−7.90 (m, 6H); IR ν_{max} 1150−950 (BF_4^-) cm^{-1}; FABMS m/z 559 ($M^+ - BF_4$), 363, 328, 286, 209. Anal. Calcd for $C_{27}H_{26}BBiF_4$: C, 50.18; H, 4.05. Found: C, 50.31; H, 3.99.

(1-Naphthyl)triphenylbismuthonium tetrafluoroborate (3n): mp 163−164 °C; ^{1}H NMR (400 MHz) δ 7.52 (dd, 1H, J = 7.0, 8.2), 7.60−7.75 (m, 12H), 7.83 (d, 6H, J = 7.0), 7.97 (d, 1H, J = 7.0), 8.07 (d, 1H, J = 8.2), 8.18 (d, 1H, J = 8.2); IR ν_{max} 1150−950 (BF_4^-) cm^{-1}; FABMS m/z 567 ($M^+ - BF_4$), 363, 336, 286, 209. Anal. Calcd for $C_{28}H_{22}BBiF_4$: C, 51.40; H, 3.39. Found: C, 51.62; H, 3.38.

(41) (a) Howthorne, M. F. *J. Am. Chem. Soc.* **1958**, *80*, 4291. (b) Brown, H. C.; Campbell, J. B. *J. Org. Chem.* **1980**, *45*, 389. (c) Chan, K. S.; Zhou, X.; Au, M. T.; Tam, C. Y. *Tetrahedron* **1995**, *51*, 3129. (d) Cullen, K. E.; Sharp, J. T. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2565. (e) Thompson, W. J.; Gaudino, J. *J. Org. Chem.* **1984**, *49*, 5237.

(42) Pitsyan, O. A.; Gurskii, M. E.; Maiorova, T. D.; Reutov, O. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1971**, 2618.

Triphenyl(2-thienyl)bismuthonium tetrafluoroborate (3o): mp 181−182 °C; ^{1}H NMR (400 MHz) δ 7.43 (dd, 1H, J = 4.5, 3.4), 7.52 (d, 1H, J = 3.4), 7.61 (t, 3H, J = 7.3), 7.68 (t, 6H, J = 7.3), 7.85−7.95 (m, 7H); IR ν_{max} 1150−900 (BF_4^-) cm^{-1}; FABMS m/z 523 ($M^+ - BF_4$), 369, 363, 286, 209. Anal. Calcd for $C_{22}H_{18}BBiF_4S$: C, 43.30; H, 2.97. Found: C, 43.57; H, 2.90.

(2-Furyl)triphenylbismuthonium tetrafluoroborate (3p): mp 154−155 °C; ^{1}H NMR (400 MHz) δ 6.72 (dd, 1H, J = 3.7, 2.1), 6.99 (d, 1H, J = 3.7), 7.60 (t, 3H, J = 7.7), 7.67 (t, 6H, J = 7.8), 7.91 (d, 1H, J = 2.1), 7.93 (d, 6H, J = 8.0); IR ν_{max} 1150−950 (BF_4^-) cm^{-1}; FABMS m/z 507 ($M^+ - BF_4$), 363, 353, 286, 276, 209. Anal. Calcd for $C_{22}H_{18}BBiF_4O$: C, 44.47; H, 3.05. Found: C, 44.65; H, 3.03.

Triphenyl(4-vinylphenyl)bismuthonium tetrafluoroborate (3q): mp 108−110 °C; ^{1}H NMR (200 MHz) δ 5.41 (d, 1H, J = 10.8), 5.85 (d, 1H, J = 17.6), 6.72 (dd, 1H, J = 17.6, 10.8), 7.55−7.85 (m, 19H); IR ν_{max} 1150−1000 (BF_4^-) cm^{-1}; FABMS m/z 543 ($M^+ - BF_4$), 389, 363, 312, 286, 209. Anal. Calcd for $C_{26}H_{22}BBiF_4$: C, 49.55; H, 3.52. Found: C, 49.69; H, 3.53.

Tris(4-methylphenyl)phenylbismuthonium tetrafluoroborate (3r): mp 149−150 °C; ^{1}H NMR (200 MHz) δ 2.44 (s, 9H), 7.49 (d, 6H, J = 8.1), 7.55−7.80 (m, 11H); IR ν_{max} 1150−900 (BF_4^-) cm^{-1}; FABMS m/z 559 ($M^+ - BF_4$), 391, 377, 300, 286, 209. Anal. Calcd for $C_{27}H_{26}BBiF_4$: C, 50.18; H, 4.05. Found: C, 50.41; H, 4.01.

Tris(4-methoxyphenyl)phenylbismuthonium tetrafluoroborate (3s): glassy solid; ^{1}H NMR (200 MHz) δ 3.85 (s, 9H), 7.21 (d, 6H, J = 8.4), 7.50−7.80 (m, 11H); IR ν_{max} 1150−950 (BF_4^-) cm^{-1}; FABMS m/z 607 ($M^+ - BF_4$), 316, 209. Anal. Calcd for $C_{27}H_{26}BBiF_4O_3$: C, 46.71; H, 3.77. Found: C, 46.79; H, 3.75.

Tris(4-chlorophenyl)phenylbismuthonium tetrafluoroborate (3t): mp 156−157 °C; ^{1}H NMR (200 MHz) δ 7.63 (d, 6H, J = 8.7), 7.65−7.80 (m, 11H); IR ν_{max} 1150−900 (BF_4^-) cm^{-1}; FABMS m/z 619 ($M^+ - BF_4$; ^{35}Cl × 3), 431, 397, 320, 286, 209. Anal. Calcd for $C_{24}H_{17}BBiCl_3F_4$: C, 40.74; H, 2.42. Found: C, 40.93; H, 2.37.

(2-Methoxyphenyl)triphenylbismuthonium trifluoromethanesulfonate (5): mp 98−99 °C; ^{1}H NMR (200 MHz) δ 3.85 (s, 3H), 7.28 (t, 1H, J = 8.1), 7.37 (d, 1H, J = 8.1), 7.58−7.83 (m, 17H); IR ν_{max} 1300−1200 (OTf^-), 1200−1100 (OTf^-) cm^{-1}; FABMS m/z 547 ($M^+ - OTf$), 393, 363, 316, 286, 209. Anal. Calcd for $C_{26}H_{22}BiF_3O_4S$: C, 44.84; H, 3.18. Found: C, 44.66; H, 3.13.

Synthesis of Triarylbismuth Dichlorides (7). General Procedure. To a solution of triarylbismuthane **6** (2.0 mmol) in CH_2Cl_2 (10 mL) was added sulfuryl chloride (0.18 mL, 2.2 mmol) at 0 °C, and the resulting mixture was stirred for 2−3 h at this temperature. The volatiles were evaporated under reduced pressure to leave dichloride **7** as a crystalline solid in a quantitative yield. (4-Chlorophenyl)(2-isopropoxyphenyl)(4-methylphenyl)bismuth dichloride (**7c**) was converted to the corresponding fluoride **8c** without purification.

(4-Chlorophenyl)(2-methoxyphenyl)(4-methylphenyl)bismuth dichloride (7a): mp 175−178 °C; ^{1}H NMR (200 MHz) δ 2.44 (s, 3H), 3.86 (s, 3H), 7.17 (t, 1H, J = 7.3), 7.22 (d, 1H, J = 7.3), 7.45−7.52 (m, 3H), 7.64 (d, 2H, J = 8.9), 7.70 (d, 1H, J = 7.3), 8.45 (d, 2H, J = 8.4), 8.58 (d, 2H, J = 8.9); FABMS m/z 553 ($M^+ - Cl$; ^{35}Cl × 2), 427, 411, 407, 351, 335, 320, 316, 300, 209. Anal. Calcd for $C_{20}H_{18}BiCl_3O$: C, 40.74; H, 3.08. Found: C, 40.65; H, 3.07.

(4-Chlorophenyl)(4-methoxyphenyl)(2-methylphenyl)bismuth dichloride (7b): mp 152−156 °C; ^{1}H NMR (200 MHz) δ 2.62 (s, 3H), 3.88 (s, 3H), 7.19 (dt, 2H, J = 9.2, 2.0), 7.32−7.48 (m, 3H), 7.65 (dt, 2H, J = 8.8, 2.0), 7.66 (d, 1H, J = 8.0), 8.59 (dt, 2H, J = 9.2, 2.0), 8.64 (dt, 2H, J = 8.8, 2.0); FABMS m/z 553 ($M^+ - Cl$; ^{35}Cl × 2), 427, 411, 407, 351, 335, 320, 316, 300, 209. Anal. Calcd for $C_{20}H_{18}BiCl_3O$: C, 40.74; H, 3.08. Found: C, 41.05; H, 3.17.

Synthesis of Triarylbismuth Difluorides (8). General Procedure. A mixture of **7** (1.0 mmol), KF (581 mg, 10 mmol), EtOH (5 mL), and water (0.25 mL) was stirred vigorously for 12 h at room temperature. The mixture was then diluted with water (5 mL), and EtOH was removed under reduced pressure. The aqueous phase was extracted with CH_2Cl_2 (5 mL × 4), and the combined organic extracts were concentrated under reduced pressure. An oily residue was again reacted with KF (290 mg, 5.0 mmol), EtOH (5 mL), and water (0.25 mL) for 6 h. A similar workup of the mixture gave a crystalline residue, which was recrystallized from CH_2Cl_2/hexane (1:5) to yield difluoride **8** as colorless crystals.

(4-Chlorophenyl)(2-methoxyphenyl)(4-methylphenyl)bismuth difluoride (8a): 66%; mp 167−170 °C (decomp); ^{1}H NMR (200 MHz) δ 2.44 (s, 3H), 3.76 (s, 3H), 7.12−7.19 (m, 2H), 7.47 (dt, 1H, J = 7, 1.4), 7.51 (d, 2H, J = 8), 7.61 (d, 2H, J = 7), 7.66 (d, 1H, J = 8), 8.12 (d, 2H, J = 8), 8.25 (d, 2H, J = 8); FABMS m/z 537 ($M^+ - F$; ^{35}Cl), 427, 411, 407, 339, 335, 320, 319, 316, 300, 209. Anal. Calcd for $C_{20}H_{18}BiClF_2O$: C, 43.14; H, 3.26. Found: C, 42.98; H, 3.25.

(4-Chlorophenyl)(4-methoxyphenyl)(2-methylphenyl)bismuth difluoride (8b): 84%; mp 119−120 °C; ^{1}H NMR (200 MHz) δ 2.60 (s, 3H), 3.86 (s, 3H), 7.20 (d, 2H, J = 9.2), 7.35−7.50 (m, 3H), 7.66 (d, 2H, J = 8.8), 7.67 (d, 1H, J = 8.8), 8.20 (d, 2H, J = 9.2), 8.27 (d, 2H, J = 8.8); FABMS m/z 537 ($M^+ - F$; ^{35}Cl), 427, 411, 407, 339, 335, 320, 319, 316, 300, 209. Anal. Calcd for $C_{20}H_{18}BiClF_2O$: C, 43.14; H, 3.26. Found: C, 42.89; H, 3.24.

(4-Chlorophenyl)(2-isopropoxyphenyl)(4-methylphenyl)bismuth difluoride (8c): 80%; mp 135−147 °C (decomp); ^{1}H NMR (200 MHz) δ 1.06 (d, 6H, J = 5.9), 2.44 (s, 3H), 4.59 (sept, 1H, J = 5.9), 7.00−7.70 (m, 8H), 8.15 (d, 2H, J = 8), 8.28 (d, 2H, J = 9); FABMS m/z; 565 ($M^+ - F$; ^{35}Cl), 455, 435, 411, 344, 320, 300, 209. Anal. Calcd for $C_{22}H_{22}BiClF_2O$: C, 45.18; H, 3.79. Found: C, 44.95; H, 3.69.

Synthesis of Bismuthonium Salts Bearing Four Different Aryl Ligands 9. These compounds were prepared from **8** by the tin or boron method similarly to the synthesis of **3**. The reaction conditions and yields of **8** are listed in Table 2.

(4-Chlorophenyl)(2-methoxyphenyl)(4-methoxyphenyl)(4-methylphenyl)bismuthonium tetrafluoroborate (9a): pasty solid; ^{1}H NMR (400 MHz) δ 2.45 (s, 3H), 3.84 (s, 3H), 3.87 (s, 3H), 7.20 (d, 2H, J = 9.0), 7.25−7.33 (m, 2H), 7.49 (d, 2H, J = 8.1), 7.57−7.75 (m, 10H); IR ν_{max} 1150−950 (BF_4^-) cm^{-1}; FABMS m/z 625 ($M^+ - BF_4$; ^{35}Cl). Anal. Calcd for $C_{27}H_{25}BBiClF_4O_2$: C, 45.50; H, 3.53. Found: C, 45.45; H, 3.49.

(4-Chlorophenyl)(2-isopropoxyphenyl)(2-methoxyphenyl)(4-methylphenyl)bismuthonium tetrafluoroborate (9b): mp 160−166 °C; ^{1}H NMR (200 MHz) δ 0.99 (d, 6H, J = 6.1), 2.47 (s, 3H), 3.86 (s, 3H), 4.72 (sept, 1H, J = 6.1), 7.2−7.8 (m, 16H); IR ν_{max} 1150−950 (BF_4^-) cm^{-1}; FABMS m/z 653 ($M^+ - BF_4$; ^{35}Cl), 455, 451, 435, 427, 411, 408, 344, 316, 300, 209. Anal. Calcd for $C_{29}H_{29}BBiClF_4O_2$: C, 47.02; H, 3.95. Found: C, 46.78; H, 3.85.

(4-Chlorophenyl)(2-methoxyphenyl)(4-methylphenyl)(4-methylthiophenyl)bismuthonium tetrafluoroborate (9c): glassy solid; ^{1}H NMR (400 MHz) δ 2.45 (s, 3H), 2.51 (s, 3H), 3.83 (s, 3H), 7.27 (dt, 1H, J = 1, 7.2), 7.30 (d, 1H, J = 8.1), 7.48 (d, 2H, J = 8.5), 7.49 (d, 2H, J = 7.3), 7.60 (d, 2H, J = 8.3), 7.60−7.68 (m, 6H), 7.70 (d, 2H, J = 8.3); IR ν_{max} 1150−900 (BF_4^-) cm^{-1}; FABMS m/z 641 ($M^+ - BF_4$; ^{35}Cl), 332, 320, 316, 300, 209. Anal. Calcd for $C_{27}H_{25}BBiClF_4OS$: C, 44.50; H, 3.46. Found: C, 44.45; H, 3.38.

(4-Chlorophenyl)(4-methoxyphenyl)(2-methylphenyl)(2-thienyl)bismuthonium tetrafluoroborate (9d): glassy solid; ^{1}H NMR (400 MHz) δ 2.50 (s, 3H), 3.87 (s, 3H), 7.19 (d, 2H, J = 8.8), 7.40 (dd, 1H, J = 4.9, 3.7), 7.43−7.64 (m, 5H), 7.64 (d, 2H, J = 8.5), 7.86 (d, 2H, J = 8.8), 7.89 (d, 2H, J = 8.5), 7.90 (d, 1H, J = 4.9); IR ν_{max} 1150−900 (BF_4^-) cm^{-1}; FABMS m/z 601 ($M^+ - BF_4$; ^{35}Cl), 320, 316, 300, 292, 209.

Anal. Calcd for $C_{24}H_{21}BBiClF_4OS$: C, 41.85; H, 3.07. Found: C, 41.74; H, 3.08.

(4-Chlorophenyl)(2-isopropoxyphenyl)(4-methoxyphenyl)(4-methylphenyl)bismuthonium tetrafluoroborate (9e): glassy solid; ^{1}H NMR (200 MHz) δ 1.02 (d, 6H, J = 5.9), 2.45 (s, 3H), 3.88 (s, 3H), 4.70 (sept, 1H, J = 5.9), 7.18−7.27 (m, 4H), 7.49 (d, 2H, J = 8.1), 7.66−7.77 (m, 10H); IR ν_{max} 1150−1000 (BF_4^-) cm^{-1}; FABMS m/z 653 ($M^+ - BF_4$; ^{35}Cl), 455, 451, 435, 427, 411, 408, 344, 316, 300, 209. Anal. Calcd for $C_{29}H_{29}BBiClF_4O_2$: C, 47.02; H, 3.95. Found: C, 46.89; H, 3.98.

(4-Chlorophenyl)(2-methoxyphenyl)(4-methoxyphenyl)-(4-methylphenyl)bismuthonium (*d*)-Camphor-10-sulfonate (10). Treatment of **9a** (356 mg, 0.499 mmol) adsorbed on silica gel with an aqueous solution (30 mL) of (*d*)-camphor-10-sulfonic acid sodium salt (2.54 g, 10 mmol) followed by extraction with CH_2Cl_2 gave the corresponding bismuthonium (*d*)-camphor-10-sulfonate **10** (273 mg, 64%) as a pasty solid. The ^{1}H NMR spectrum of **10** in $CDCl_3$ showed no diastereotopic peaks. Added europium tris(heptafluorobutanoylpivaloylmethanate) failed to cause the peak separation: ^{1}H NMR (200 MHz) δ 0.65 (s, 3H), 0.96 (s, 3H), 1.11−2.28 (m, 7H), 2.41 (s, 3H), 2.45−2.85 (m, 2H), 3.74 (s, 3H), 3.84 (s, 3H), 7.09−7.85 (m, 16H); IR ν_{max} 1383 (SO_2), 1181 (SO_2) cm^{-1}; FABMS m/z 625 ($M^+ - OSO_2R$; ^{35}Cl). Although spectroscopic data supported a high state of purity of **10**, we could not obtain the satisfactory analytical data within an accuracy of ±0.4%.

[2-(4,4-Dimethyl-3,4-dihydrooxazol-2-yl)phenyl]bis(4-methoxyphenyl)bismuthane (11). To a mixture of tris(4-methoxyphenyl)bismuthane (2.65 g, 5.0 mmol), HMPA (1.78 mL, 10.2 mmol), MeOH (1 mL), and CH_2Cl_2 (30 mL) was added Me_3SiOTf (0.99 mL, 5.2 mmol) at 0 °C, and the resulting solution was stirred for 2 h at room temperature. The volatiles were removed under reduced pressure, and an oily residue was thoroughly dried under vacuum to leave a colorless solid. At −20 °C, a THF solution (20 mL) of this solid was added slowly to a solution of 2-(4,4-dimethyl-3,4-dihydrooxazol-2-yl)phenylmagnesium bromide, generated from 1-bromo-2-(4,4-dimethyl-3,4-dihydrooxazol-2-yl)benzene (1.91 g, 7.5 mmol), magnesium (194 mg, 8.0 mmol), and THF (35 mL). The resulting mixture was stirred for 15 min, during which time it was warmed to room temperature. The mixture was then poured into a saturated aqueous NH_4Cl solution (40 mL) at 0 °C. The organic phase was separated, and the aqueous phase was extracted with benzene (20 mL × 2). The combined organic extracts were washed with brine (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure to leave an oily residue, which was crystallized from benzene/MeOH (1:4) to give bismuthane **11** as a colorless crystalline solid (2.21 g, 73%): mp 139−141 °C; ^{1}H NMR (200 MHz) δ 1.14 (s, 6H), 3.78 (s, 6H), 3.98 (s, 2H), 6.88 (d, 4H, J = 8.5), 7.22−7.46 (m, 2H), 7.62 (d, 4H, J = 8.5), 7.82 (d, 1H, J = 7.0), 7.99 (d, 1H, J = 7.3). Anal. Calcd for $C_{25}H_{26}BiNO_3$: C, 50.26; H, 4.39; N, 2.34. Found: C, 50.33; H, 4.32; N, 2.37.

[2-(4,4-Dimethyl-3,4-dihydrooxazol-2-yl)phenyl](4-methoxyphenyl)(4-trifluoromethylphenyl)bismuthane (12). This compound was synthesized from bismuthane **11** (1.79 g, 3.0 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.63 mL, 4.5 mmol) according to a similar procedure used for the preparation of **11**. Bismuthane **12** was obtained as a colorless crystalline solid (1.14 g, 60%) by fractional recrystallization from benzene/MeOH (1:4): mp 148−150 °C; ^{1}H NMR (200 MHz) δ 1.11 (s, 3H), 1.13 (s, 3H), 3.78 (s, 3H), 4.00 (s, 2H), 6.90 (d, 2H, J = 8.3), 7.33 (t, 1H, J = 7.0), 7.42 (t, 1H, J = 7.5), 7.53 (d, 2H, J = 7.6), 7.60 (d, 2H, J = 8.3), 7.79 (d, 1H, J = 7.3), 7.85 (d, 2H, J = 7.6), 8.01 (d, 1H, J = 7.3); IR ν_{max} 1649 (C═N) cm^{-1}; FABMS m/z 528, 490, 383, 209. Anal. Calcd for $C_{25}H_{23}BiF_3NO_2$: C, 47.25; H, 3.65; N, 2.20. Found: C, 47.36; H, 3.47; N, 2.18.

[2-(4,4-Dimethyl-3,4-dihydrooxazol-2-yl)phenyl](4-methoxyphenyl)(4-trifluoromethylphenyl)bismuth Difluoride (13). To a 50 mL Teflon reaction vessel containing bismuthane **12** (0.95 g, 1.5 mmol), CH_2Cl_2 (5 mL), and CH_3CN (5 mL) was added xenon difluoride (0.25 g, 1.5 mmol) at −20 °C. The mixture was stirred for 2 h, during which time it was warmed to room temperature. Evaporation of the solvents under reduced pressure left an oily residue, which was crystallized from CH_2Cl_2/hexane (1:10) to yield difluoride **13** (0.88 g, 87%) as a colorless solid: mp 199−201 °C (decomp); ^{1}H NMR (200 MHz) δ 0.93 (s, 6H), 3.86 (s, 3H), 4.15 (s, 2H), 7.16 (d, 2H, J = 9.0), 7.52−7.76 (m, 3H), 7.88 (d, 2H, J = 7.8), 8.08 (dd, 1H, J = 7.3, 1.4), 8.19 (d, 2H, J = 9.0), 8.43 (d, 2H, J = 7.8); FABMS m/z 654 ($M^+ - F$), 528, 490, 402, 383, 209. Anal. Calcd for $C_{25}H_{23}BiF_5NO_2$: C, 44.59; H, 3.44; N, 2.08. Found: C, 44.80; H, 3.33; N, 2.06.

Synthesis of Unsymmetrical Tetraarylbismuthonium Salts Bearing the Oxazoline Group (14). These compounds were synthesized from difluoride **13**, $BF_3{\cdot}OEt_2$, and boronic acids **4b**,**l** according to a similar procedure (boron method) used for the preparation of **3**.

[2-(4,4-Dimethyl-3,4-dihydrooxazol-2-yl)phenyl](4-methylphenyl)(4-methoxyphenyl)(4-trifluoromethylphenyl-)bismuthonium tetrafluoroborate (14a): glassy solid (97%); ^{1}H NMR (400 MHz) δ 0.74 (s, 3H), 0.76 (s, 3H), 2.44 (s, 3H), 3.87 (s, 3H), 4.22 (s, 2H), 7.19 (d, 2H, J = 8.8), 7.48 (d, 2H, J = 8.0), 7.60 (d, 2H, J = 8.0), 7.64 (d, 2H, J = 8.8), 7.6−7.7 (m, 1H), 7.76−7.85 (m, 2H), 7.86 (s, 4H), 8.29 (dd, 1H, J = 7.0, 2); IR ν_{max} 1646 (C═N), 1100−950 (BF_4^-) cm^{-1}; FABMS m/z 726 ($M^+ - BF_4$), 528, 490, 474, 383, 209. Anal. Calcd for $C_{32}H_{30}BBiF_7NO_2$: C, 47.25; H, 3.72; N, 1.72. Found: C, 47.04; H, 3.76; N, 1.68.

[2-(4,4-Dimethyl-3,4-dihydrooxazol-2-yl)phenyl](4-methoxyphenyl)(2-thienyl)(4-trifluoromethylphenyl)bismuthonium tetrafluoroborate (14b): crystals (72%), mp 224−226 °C; ^{1}H NMR (400 MHz) δ 0.77 (s, 3H), 0.84 (s, 3H), 3.88 (s, 3H), 4.25 (s, 2H), 7.20 (d, 2H, J = 9.0), 7.38 (dd, 1H, J = 3.6, 4.9), 7.49 (d, 1H, J = 3.6), 7.75−7.85 (m, 6H), 7.89 (d, 2H, J = 8.0), 8.02 (d, 2H, J = 8.0), 8.29 (m, 1H); IR ν_{max} 1638 (C═N), 1200−1000 (BF_4^-) cm^{-1}; FABMS m/z 718 ($M^+ - BF_4$), 528, 490, 466, 383, 209. Anal. Calcd for $C_{29}H_{26}BBiF_7NO_2S$: C, 43.25; H, 3.25; N, 1.74. Found: C, 43.16; H, 3.07; N, 1.74.

[2-(4,4-Dimethyl-3,4-dihydrooxazol-2-yl)phenyl](4-methoxyphenyl)(2-thienyl)(4-trifluoromethylphenyl)bismuthonium Tosylate (15). A mixture of **14b** (0.19 g, 0.23 mmol), tetraethylammonium tosylate (0.69 g, 2.3 mmol), and CH_2Cl_2 (10 mL) was stirred at room temperature for 8 h. Water (10 mL) was then added, and the organic phase separated was again treated with the ammonium tosylate (0.69 g, 2.3 mmol) for 16 h. The separated organic phase was dried over $MgSO_4$ and concentrated under reduced pressure to leave an oily residue, which was washed with CH_2Cl_2/Et_2O (1:2) to yield bismuthonium tosylate **15** as a pasty solid (0.17 g, 83%): ^{1}H NMR (400 MHz) δ 0.80 (s, 3H), 0.83 (s, 3H), 2.28 (s, 3H), 3.85 (s, 3H), 4.13 (s, 2H), 6.89 (d, 2H, J = 8.1), 7.10 (d, 2H, J = 9.0), 7.20 (d, 2H, J = 8.1), 7.26 (m, 1H), 7.41 (d, 1H, J = 3.2), 7.54−7.62 (m, 2H), 7.68−7.80 (m, 2H), 7.75 (d, 2H, J = 8.1), 8.00−8.10 (m, 3H), 8.14 (d, 2H, J = 7.9); IR ν_{max} 1646 (C═N), 1325 (SO_2), 1168 (SO_2) cm^{-1}; FABMS m/z 718 ($M^+ - OTs$), 528, 490, 466, 383, 209. Although spectroscopic data supported a high state of purity of **15**, we could not obtain the analytical data within an accuracy of ±0.4%.

Synthesis of [2-(4,4-Dimethyl-3,4-dihydrooxazol-2-yl)-phenyl](4-methoxyphenyl)(2-thienyl)(4-trifluoromethylphenyl)bismuthonium Halides (16). General Procedure. A mixture of **15** (55 mg, 0.062 mmol), a saturated aqueous NaX solution (10 mL, X = Cl, Br, I), and CH_2Cl_2 (5 mL) was stirred for 10 min at room temperature. The organic phase was then separated and treated with a new portion of saturated aqueous NaX solution (10 mL). The separated organic phase was dried over $MgSO_4$ and concentrated under reduced pressure to leave an oily residue, which was crystallized from CH_2Cl_2/hexane (1:4) to give bismuthonium halide

16 as a colorless (**16a**) or pale yellow (**16b**) solid. Iodide **16c** was obtained as a yellow solid that was approximately 95% pure (based on ^{1}H NMR).

Chloride (16a): 58%, mp 142−144 °C; ^{1}H NMR (400 MHz) δ 0.86 (s, 3H), 0.88 (s, 3H), 3.84 (s, 3H), 4.13 (s, 2H), 7.06 (d, 2H, J = 9.1), 7.15−7.28 (m, 2H), 7.58 (dt, 1H, J = 1.3, 7.6), 7.62−7.68 (m, 2H), 7.75 (d, 2H, J = 8.1), 7.81 (d, 1H, J = 7.6), 8.10 (dd, 1H, J = 7.6, 1.3), 8.30 (br-d, 2H), 8.39 (br-d, 2H); IR ν_{max} 1646 (C═N) cm^{-1}; FABMS m/z 718 (M^+ − Cl), 490, 466, 383, 209. Anal. Calcd for $C_{29}H_{26}BiClF_3NO_2S$: C, 46.19; H, 3.48; N, 1.86. Found: C, 45.98; H, 3.75; N, 1.69.

Bromide (16b): 53%, mp 133−135 °C; ^{1}H NMR (400 MHz) δ 0.89 (s, 3H), 0.90 (s, 3H), 3.85 (s, 3H), 4.14 (s, 2H), 7.06 (d, 2H, J = 9.0), 7.19 (dd, 1H, J = 4.7, 3.5), 7.27 (d, 1H, J = 3.5), 7.58 (dt, 1H, J = 1.3, 7.6), 7.63−7.72 (m, 2H), 7.75 (d, 2H, J = 8.3), 7.80 (d, 1H, J = 7.5), 8.10 (dd, 1H, J = 7.1, 1.2), 8.28 (br-d, 2H), 8.36 (br-d, 2H); IR ν_{max} 1646 (C═N) cm^{-1}; FABMS m/z 718 (M^+ − Br), 528, 490, 466, 383, 209. Anal. Calcd for $C_{29}H_{26}BiBrF_3NO_2S$: C, 43.62; H, 3.28; N, 1.75. Found: C, 43.86; H, 3.05; N, 1.71.

Iodide (16c): ^{1}H NMR (400 MHz) δ 0.89 (s, 3H), 0.90 (s, 3H), 3.85 (s, 3H), 4.18 (s, 2H), 7.08 (d, 2H, J = 8.8), 7.23 (dd, 1H, J = 4.7, 3.5), 7.36 (d, 1H, J = 3.5), 7.62 (t, 1H, J = 7.6), 7.65−7.72 (m, 2H), 7.76 (d, 2H, J = 7.9), 7.79 (d, 1H, J = 7.5), 8.13 (m, 1H), 8.16 (d, 2H, J = 8.8), 8.27 (d, 2H, J = 7.6); FABMS m/z 718 (M^+ − I), 528, 490, 466, 383, 209.

VT-NMR Measurement. Bismuthonium salt **14**, **15**, or **16a**,**b** was dissolved in a solvent in an NMR tube under an argon atmosphere, and the tube was sealed with a cap. The coalescence temperatures (T_c) of the geminal oxazoline-methyl peaks are summarized in Table 5. Activation energies at T_c for the permutation of **16a**,**b** were calculated from the equation $\Delta G^{\ddagger}_{T_c} = 4.57 \times 10^{-3} T_c[10.32 + \log(T_c\sqrt{2}/\pi\Delta\nu)]$.[43] The other $\Delta G^{\ddagger}$ threshold values in Table 5 were estimated by assuming that the *gem*-methyl peaks had coalesced at the highest observable temperatures in the respective solvents (135 °C in DMSO-d_6; 110 °C in pyridine-d_5; 150 °C in 1,2-dichlorobenzene-d_4). When allowed to stand in 1,2-dichlorobenzene-d_4, chlorobenzene-d_5, or toluene-d_8, **16a**,**b** decomposed to (4-methoxyphenyl)(2-thienyl)(4-trifluoromethylphenyl)bismuthane **17** and the corresponding haloarenes **18a**,**b** in a quantitative NMR yield. Unsymmetrical bismuthane **17** could not be isolated, because it underwent facile disproportionation during attempted purification by recrystallization and column chromatography. It was therefore characterized on the basis of the ^{1}H NMR and FABMS data of a crude product. Compounds **18a**,**b** were identified by direct comparison with the authentic specimens.

Bismuthane 17: ^{1}H NMR (400 MHz; in 1,2-dichlorobenzene-d_4) δ 3.60 (s, 3H, OMe), 6.84 (d, 2H, J = 8.3, $MeOC_6H_4$), 7.08 (dd, 1H, J = 4.6, 3.5, C_4H_3S), 7.29 (d, 1H, J = 3.5, C_4H_3S), 7.46 (d, 2H, J = 8.3, $MeOC_6H_4$), 7.54 (d, 1H, J = 4.6, C_4H_3S), 7.63 (d, 2H, J = 7.8, $CF_3C_6H_4$), 7.82 (d, 2H, J = 7.8, $CF_3C_6H_4$); FABMS m/z 461 [(4-$MeOC_6H_4$)(4-$CF_3C_6H_4$)Bi$^+$], 437 [(4-$CF_3C_6H_4$)(2-C_4H_3S)Bi$^+$], 399 [(4-$MeOC_6H_4$)(2-C_4H_3S)Bi$^+$], 209 (Bi$^+$).

[2-(4,4-Dimethyl-3,4-dihydrooxazol-2-yl)phenyl]bis(4-methylphenyl)bismuth Difluoride (19). This compound was synthesized from [2-(4,4-dimethyl-3,4-dihydrooxazol-2-yl)-phenyl]bis(4-methylphenyl)bismuthane[44] (766 mg, 1.4 mmol) and xenon difluoride (237 mg, 1.4 mmol) according to a similar procedure used for the synthesis of **13**. Yield: 830 mg, 98%; mp 184−187 °C (decomp); ^{1}H NMR (400 MHz) δ 0.92 (s, 6H), 2.40 (s, 6H), 4.10 (s, 2H), 7.45 (d, 4H, J = 8.0), 7.53 (dt, 1H, J = 1.6, 7.4), 7.60−7.76 (m, 2H), 8.05 (dd, 1H, J = 1.2, 7.6), 8.13 (d, 4H, J = 8.0); IR ν_{max} 1653 (C═N) cm^{-1}; FABMS m/z 584 (M^+ − F), 474, 402, 383, 300, 209. Anal. Calcd for $C_{25}H_{26}BiF_2NO$: C, 49.76; H, 4.34; N, 2.32. Found: C, 49.62; H, 4.24; N, 2.37.

[2-(4,4-Dimethyl-3,4-dihydrooxazol-2-yl)phenyl]tris(4-methylphenyl)bismuthonium Tetrafluoroborate (20). This compound was prepared from **19** (301 mg, 0.50 mmol), **4b** (68 mg, 0.50 mmol), and BF_3·OEt_2 (65 μL, 0.50 mmol) according to a similar procedure (boron method) used for the synthesis of **3**. Yield: 340 mg, 91%; mp 216−218 °C; ^{1}H NMR (400 MHz) δ 0.75 (s, 6H), 2.44 (s, 9H), 4.22 (s, 2H), 7.46 (d, 6H, J = 7.8), 7.54 (d, 6H, J = 7.8), 7.64 (d, 1H, J = 7.3), 7.73−7.90 (m, 2H), 8.30 (d, 1H, J = 7); ^{13}C NMR (50 MHz) δ 21.60, 27.58, 68.11, 81.39, 130.32, 131.14, 132.88, 133.11, 134.99, 135.59, 136.52, 137.73, 139.22, 142.88, 163.09; IR ν_{max} 1646 (C═N), 1150−975 (BF_4^-) cm^{-1}; FABMS m/z 656 (M^+ − BF_4), 474, 383, 300, 209. Although spectral data supported a high state of purity of compound **20**, satisfactory analytical results were not available probably due to the persistent adhesion of the solvent used for recrystallization.

[2-(4,4-Dimethyl-3,4-dihydrooxazol-2-yl)phenyl]tris(4-methylphenyl)bismuthonium Bromide (21). A mixture of **20** (132 mg, 0.178 mmol), a saturated aqueous NaBr solution (10 mL), and CH_2Cl_2 (5 mL) was vigorously stirred for 5 min at room temperature, and the aqueous layer was removed by decantation. This treatment was repeated twice, and then the separated organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. Recrystallization of an oily residue from CH_2Cl_2/hexane (1:2) yielded bromide **21** as a pale yellow solid (90 mg, 69%): mp 113−115 °C; ^{1}H NMR (400 MHz) δ 0.78 (s, 6H), 2.42 (s, 9H), 4.16 (s, 2H), 7.41 (d, 6H, J = 8.1), 7.69 (d, 6H, J = 8.1), 7.7−7.8 (m, 3H), 8.18−8.28 (m, 1H); ^{13}C NMR (50 MHz) δ 21.59, 27.72, 68.14, 81.24, 129.54, 130.81, 131.26, 132.46, 132.56, 135.24, 135.45, 135.91, 137.52, 142.31, 162.93; IR ν_{max} 1646 (C═N) cm^{-1}; FABMS m/z 656 (M^+ − Br), 474, 383, 300, 209. Anal. Calcd for $C_{32}H_{33}BiBrNO$: C, 52.19; H, 4.52; N, 1.90. Found: C, 51.56; H, 4.47; N, 1.78.

Thermal Decomposition of Bromide 21. A solution of bromide **21** in a deuterio solvent was monitored by ^{1}H NMR at a given temperature. Bismuthane **22** and bromoarene **18b** were formed quantitatively. The methyl groups on the oxazoline ring in **21** and **18b** were used for the estimation of rate constants. A half-life period of **21** did not depend on its concentration over 0.005−0.035 M. Compound **22**: ^{1}H NMR (200 MHz) δ 2.32 (s, 9H), 7.18 (d, 6H, J = 7.6), 7.62 (d, 6H, J = 7.6); ^{1}H NMR (200 MHz; in 1,2-dichlorobenzene-d_4) δ 2.20 (s, 9H), 7.07 (d, 6H, J = 7.4), 7.62 (d, 6H, J = 7.4). Compound **18b**: ^{1}H NMR (200 MHz) δ 1.41 (s, 6H), 4.13 (s, 2H), 7.20−7.37 (m, 2H), 7.57−7.72 (m, 2H).

X-ray Diffraction Analysis of Compound 20. A colorless crystal of dimensions 0.14 × 0.14 × 0.20 mm, grown from CH_2Cl_2/Et_2O (1:2) at room temperature, was used for X-ray diffraction. Data were recorded on a Rigaku AFC7S diffractometer, with graphite-monochromated Mo Kα (λ = 0.71069 Å) radiation, using the $\omega-2\theta$ scan technique to a maximum 2θ value of 55.3°. Scans of (0.94 + 0.30 tan θ)° were made at a speed of 4.0° min^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.92 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The structure was solved by the Patterson methods[45] and expanded using the Fourier techniques.[46] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral atom scattering factors were taken from

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Cromer and Waber.[47] Anomalous dispersion effects were included in F_{calc};[48] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[49] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[50] All calculations were performed using the teXsan[51] crystallographic software package of Molecular Structure Corporation. Further details are provided as Supporting Information.

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Supporting Information Available: Tables of experimental details for an X-ray diffraction study, atomic coordinates, thermal parameters, bond distances and angles, torsion angles, nonbonded contacts, and figures giving additional views and unit cell packing for **20**, and full IR data (ν_{max}) of all the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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