

First synthesis, X-ray structure analysis and reactions of alkenyltriphenylbismuthonium salts

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Treatment of triphenylbismuth difluoride with alkenyltrimethylsilanes **1** or trimethylsilyl cyanide-alkenyltrialkylstannanes **3** in the presence of boron trifluoride-diethyl ether gave the corresponding alkenyltriphenylbismuthonium tetrafluoroborates **2** in moderate to good yields. An X-ray crystallographic analysis of the salt **2e** confirmed the distorted tetrahedral geometry of the central bismuth atom. When treated with a sulfinate **5** or the thiolate **11**, the salts **2** readily transferred both the vinyl and phenyl moieties to these nucleophiles to afford the sulfones **7–10** or the sulfides **12, 13**, respectively. In the presence of a palladium catalyst, the salt **2e** underwent the Heck-type reaction with ethyl acrylate **17** to afford the dienoate **18** and cinnamate **19** in moderate yields. Action of KOBu' on the salt **2b** yielded *p*-tolylacetylene **22**, while a similar reaction with the salt **2e** in the presence of the styrenes **23** gave the cyclopropanes **24**. A Hammett study of the latter reaction has suggested a possible involvement of an alkylidene-carbene as the intermediate in these base-promoted reactions.

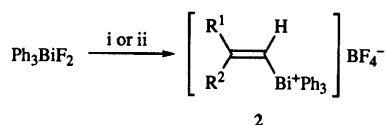
Introduction

Onium salts with a vinylic function on the central cationic atom have been receiving continued interest from both heteroatom and olefinic carbon chemistry. Although many examples derived from a variety of typical elements were reported, the literature to date contains no example of vinylbismuthonium compounds. Recently, we have developed an efficient methodology for the synthesis of 2-oxoalkyl-,^{1,2} 3-oxoalkyl-³ and allyl-triarylbismuthonium salts,⁴ which involves the reaction of triarylbismuth difluorides with silyl enolates, siloxycyclopropanes and allylsilanes, respectively, in the presence of an appropriate Lewis acid. High leaving ability of the triphenylbismuthonium group in these salts is well reflected by their enhanced reactivity towards nucleophiles and bases. As part of our systematic study on the chemistry of functionalized alkylbismuthonium compounds, we report herein the first synthesis, structure and reactions of alkenyltriphenylbismuthonium salts **2**. Compounds **2** have a distorted tetrahedral geometry around the bismuth centre and readily transfer their organyl group to S-nucleophiles and palladium complexes. The abstraction of a proton from salts **2** generates an alkylidene-carbene with simultaneous elimination of the triphenylbismuthonium group.

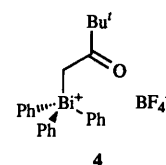
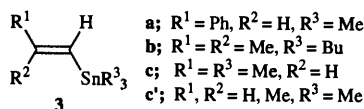
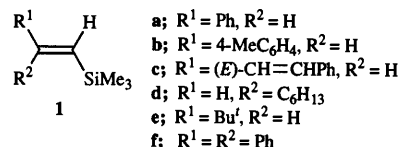
Results and discussion

Synthesis of alkenyltriphenylbismuthonium salts **2**

We synthesized the title compounds in moderate to good yields by refluxing triphenylbismuth difluoride, boron trifluoride-diethyl ether (BF₃·OEt₂) and alkenyltrimethylsilanes **1** in dichloromethane (CH₂Cl₂) for 12–25 h (Scheme 1 and Table 1). The use of a Lewis acid was indispensable for promoting the reaction. Small amounts of tetraphenylbismuthonium tetrafluoroborate was an accompanying by-product. The salts **2** were obtained in pure form by fractional recrystallization and/or column chromatography. Bulky 3,3-dimethylbut-1-enyl and 2,2-diphenylethenyl groups could not be attached to the bismuth atom, probably for steric reason (runs 5 and 6). In order to develop more efficient methodology leading to the



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| a; R ¹ = Ph, R ² = H | d; R ¹ = H, R ² = C ₆ H ₁₃ |
| b; R ¹ = 4-MeC ₆ H ₄ , R ² = H | e; R ¹ = R ² = Me |
| c; R ¹ = (<i>E</i>)-CH=CHPh, R ² = H | f; R ¹ = Me, R ² = H |
| | f'; R ¹ , R ² = H, Me |



Scheme 1 Reagents and conditions: i, BF₃·OEt₂, CH₂Cl₂, 0 °C to room temp., 1 h; alkenyltrimethylsilane **1**, reflux, 12–25 h; ii, BF₃·OEt₂, CH₂Cl₂, 0 °C to room temp., 1 h; Me₃SiCN, room temp., 1 h; alkenyltrialkylstannane **2**, room temp., 12 h

salts **2** under milder conditions, we next employed an alkenyltrialkylstannane **3** in place of an alkenylsilane **1**, since the C–Sn bond of the stannane **3** is expected to be more susceptible to cleavage than is the C–Si bond of the silane **1**. Thus, successive treatment of triphenylbismuth difluoride with trimethylsilyl cyanide (Me₃SiCN) and alkenylstannanes **3** in CH₂Cl₂ in the presence of BF₃·OEt₂ at room temperature readily gave the alkenylbismuthonium salts **2** in the pure state (Table 1, runs 7–10). The reaction proceeded in a stereospecific manner with retention of the geometry around the olefinic bond (runs 9 and 10). The addition of Me₃SiCN was essential for obtaining the pure salts **2**; in the absence of Me₃SiCN, the salts

Table 1 Alkenyltriphenylbismuthonium salts **2** obtained

Run	Silane 1 (tin 3)	Reaction conditions	Bismuthonium salt 2	Yield (%) ^a
1	1a	Reflux, 23 h	2a (R ¹ = Ph, R ² = H)	60
2	1b	Reflux, 16 h	2b (R ¹ = 4-MeC ₆ H ₄ , R ² = H)	80
3	1c	Reflux, 25 h	2c [R ¹ = (<i>E</i>)-CH=CHPh, R ² = H]	80
4	1d	Reflux, 12 h	2d (R ¹ = H, R ² = C ₆ H ₁₃)	71
5	1e	Reflux, 15 h	<i>b</i>	
6	1f	Reflux, 20 h	<i>b</i>	
7	3a	Room temp., 12 h	2a	64
8	3b	Room temp., 12 h	2e (R ¹ = R ² = Me)	84
9	3c	Room temp., 12 h	2f (R ¹ = Me, R ² = H)	60
10	3c'	Room temp., 12 h	2f' (R ¹ , R ² = H, Me) ^d	51

^a Isolated yield. ^b No alkenylbismuthonium salt was obtained. ^c An *E/Z*-mixture. Isomer ratio was 13/87. ^d An *E/Z*-mixture. Isomer ratio was 15/85.

2 were always accompanied by small amounts of tetraphenylbismuthonium tetrafluoroborate.† All the salts **2** are thermally stable in the solid state and readily dissolved in common polar solvents such as CH₂Cl₂, chloroform and acetonitrile.

Alkenyltriphenylbismuthonium tetrafluoroborates **2** exhibited some characteristic spectral features. In fast-atom bombardment (FAB) mass spectra, a strong peak due to the M⁺ - BF₄ fragment was observed. The observation of metastable peaks due to both Ph₂Bi⁺ and Ph(CH=CR¹R²)Bi⁺ fragments suggests a slight difference of the bond-dissociation energies between the Bi-C_{Ph} and Bi-C_{alkenyl} bonds. The IR spectra displayed broad intense absorption characteristic of tetrafluoroborate ion around 1150–950 cm⁻¹. The ¹³C NMR spectra showed a signal of the β-vinyl carbon at δ_c 151.7–160.0. A low chemical shift of this carbon as compared with those of the α-vinyl and phenyl carbons indicates that the positive charge on the bismuth atom may partly be diffused into the vinyl function through the π-orbital of the carbon-carbon double bond. These spectral features are consistent with the onium nature of the bismuth centre of the salts **2**.

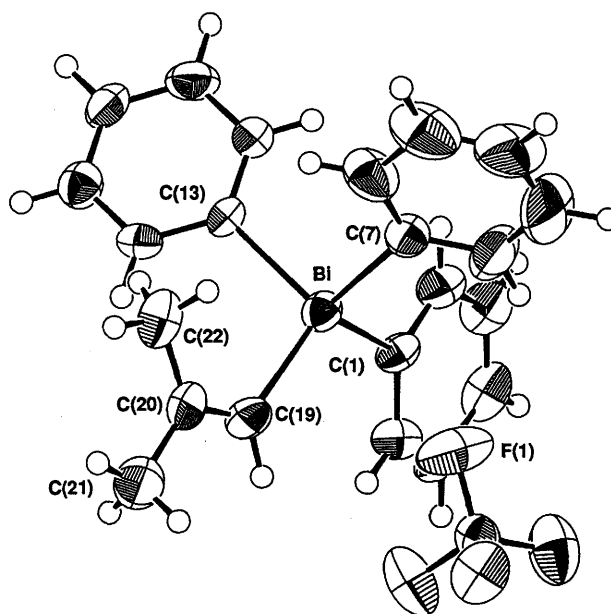
X-Ray structure analysis of compound **2e**

The crystal structure of alkenylbismuthonium salt **2e** was established by X-ray analysis. As shown in Fig. 1 and Table 2, the bismuth centre has a distorted tetrahedral geometry with the bond angles C–Bi–C 103.8(3)–115.3(3)° and the bond lengths Bi–C 2.182(9)–2.218(8) Å, which clearly endorse the onium nature of this molecule. The C–Bi–C bond angle open to the counter-anion side [C(7)–Bi–C(19) 115.5(3)°] is considerably larger than the expected value for an sp³ configuration (109° 28'), while the angle remote from the anion [C(1)–Bi–C(13) 103.8(3)°] is appreciably reduced. All the atoms bound to the carbon-carbon double bond lie on almost the same plane, and the length of the C(19)–C(20) [1.32(1) Å] bond is almost the same as that expected for the normal carbon-carbon double bond. The Bi–C(19)–C(20) and C(19)–C(20)–C(22) angles [124.1(7)° and 125.2(9)°] are slightly larger than the expected value (120°) for an sp² configuration, probably due to steric reasons. It is noteworthy that the distance between the bismuth and the nearest fluorine atoms [Bi...F(1) 3.131(6) Å] is much shorter than that [3.48(1) Å] of the known fluoroborate **4**, where the carbonyl group weakly coordinates to the cationic bismuth centre.² The absence of such coordination in salt **2e** may be the reason for the closer location of fluoroborate ion to the bismuth centre. This may in part be attributed to the difference in packing mode between the onium salts **2e** and **4**. The present

† The NMR monitoring of a CDCl₃ solution of triphenylbismuth difluoride, BF₃·OEt₂ and Me₃SiCN at room temperature has confirmed the intermediate formation of equimolar amounts of cyanotriphenylbismuthonium compound [Ph₃BiCN·X; δ_H 7.6–7.9 (9 H, m) and 8.25 (6 H, d, *J* 8.1)] and Me₃SiF [δ_H 0.23 (9 H, d, *J*_{H,F} 7.3)]. Stang *et al.* recently observed the formation of cyano(phenyl)iodonium triflate from the four-component reaction of iodobenzene, trimethylsilyl triflate, trimethylsilyl cyanide and an organotin compound.⁵

Table 2 Selected bond lengths (Å) and angles (°) for compound **2e**, with estimated standard deviation in parentheses

Bond length		Bond angle	
Bi–C(1)	2.218(8)	C(1)–Bi–C(7)	109.6(3)
Bi–C(7)	2.212(8)	C(1)–Bi–C(13)	103.8(3)
Bi–C(13)	2.204(7)	C(1)–Bi–C(19)	113.9(3)
Bi–C(19)	2.182(9)	C(7)–Bi–C(13)	106.2(3)
C(19)–C(20)	1.32(1)	C(7)–Bi–C(19)	115.3(3)
C(20)–C(21)	1.50(1)	C(13)–Bi–C(19)	107.0(3)
C(20)–C(22)	1.50(1)	Bi–C(19)–C(20)	124.1(7)
Bi...F(1)	3.131(6)	C(19)–C(20)–C(21)	120(1)
		C(19)–C(20)–C(22)	125.2(9)
		C(21)–C(20)–C(22)	114.5(9)

**Fig. 1** ORTEP drawing of compound **2e** with the atomic numbering scheme

X-ray analysis provides the first structural characterization of a bismuth compound having the Bi–C_{alkenyl} bonding.

Reactions of alkenylbismuthonium salts **2** with some nucleophiles

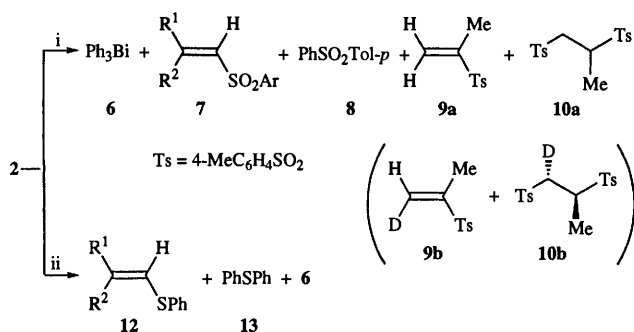
In contrast to the alkylbismuthonium derivatives, alkenylbismuthonium salts **2** did not react with neutral heteroatom nucleophiles such as dimethyl sulfide, triphenylphosphane and piperidine. However, the salts **2** smoothly underwent the C–S coupling with hydrated sodium sulfonates **5** in dimethylformamide (DMF) at room temperature (Table 3). In the reaction of salts **2a–c** with excess of sulfonates **5a,b**, the alkenyl group was preferentially transferred to the nucleophile at the α-position with retention of the olefinic geometry to give the corresponding vinyl aryl sulfones **7a–c**, together with

Table 3 Reaction of salts **2** with S-nucleophiles **5** and **11**

Run	Salt	Nu; ^a	Conditions	Product (%) ^b
1	2a	5a	Room temp., 2 h	6 (87) and 7a (94)
2	2b	5b	Room temp., 2 h	6 (94) and 7b (92)
3	2c	5b	Room temp., 2 h	6 (80) and 7c (67)
4	2e	5a	Room temp., 12 h	6 (74), 7d (43) and 8 (9)
5	2f	5a^c	Room temp., 12 h	6 (77) and 7e (66)
6	2f	5a	Room temp., 12 h	6 (73), 7e (15), 8 (4), 9a (22) and 10a (16)
7	2f	5a^d	Room temp., 12 h	6 (92), 7e (9), 8 (4), 9b (24) and 10b (21)
8	2e	11	-50 °C to room temp., 12 h	6 (47), 12a (32) and 13 (29)
9	2f	11	-50 °C to room temp., 12 h	6 (62), 12b (40) and 13 (29)

^a Ten mol equiv. of hydrated sulfinate **5** or 1 mol equiv. of thiolate **11** were used unless otherwise noted. ^b Numeral in parenthesis refers to isolated yield based on salt **2** used. ^c One mol equiv. of hydrated sulfinate **5a** was used. ^d Ten mol equiv. of anhydrous sulfinate **5a'** and 40 mol equiv. of D₂O were used.

triphenylbismuthane **6** (runs 1–3). The salt **2e** also transferred its alkenyl group predominantly (run 4). Reactivity of the salt **2f** toward sulfinate was somewhat complicated; salt **2f** reacted with an equimolar amount of sulfinate **5a** to give only α -substituted sulfone **7e**, while with an excess of the sulfinate it afforded four sulfones **7e**, **8**, **9a** and **10a** (run 6).[‡] It is likely that the sulfones **7e** and **9a** arose from the α - and β -attack of the sulfinate **5a** on the vinyl function. Since the latter type of product was not formed in the reaction of salts **2a–c,e**, both the electronic and steric factors around the olefinic carbons should be important for controlling the direction of attack of the nucleophile. These results may be understood that the salt **2f** initially undergoes metathesis with sulfinate **5a** to form an unstable adduct **14** as intermediary species, which then leads to α -substituted vinyl sulfone **7e** through the intramolecular ligand coupling (Scheme 3). Formation of compound **10a** is of interest,

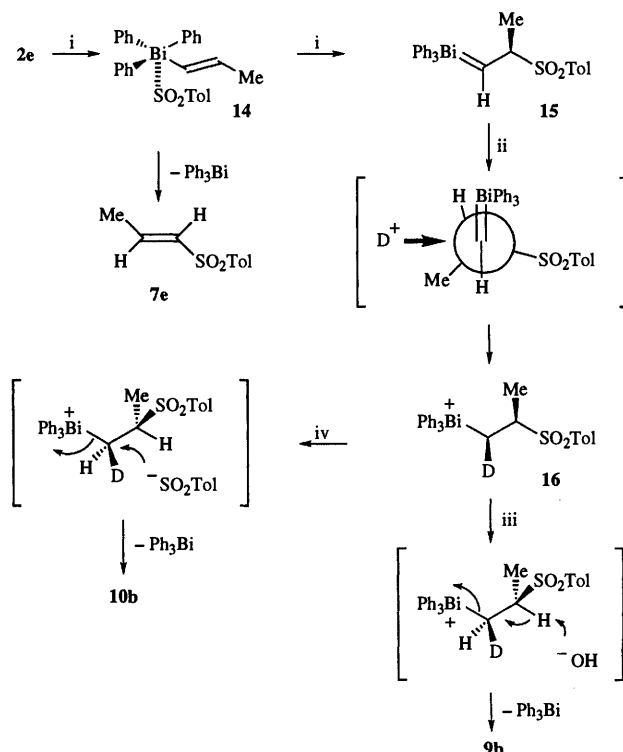


Scheme 2 Reagents and conditions: i, ArSO₂Na·(H₂O)_n, **5** (**a**; Ar = 4-MeC₆H₄, n = 4. **a'**; Ar = 4-MeC₆H₄, n = 0. **b**; Ar = Ph, n = 2), DMF, room temp., 2–12 h. ii, PhSNa, **11**, THF, -50 °C to room temp., 12 h

since it could not be obtained by the interaction between sulfone **7e** or **9a** and sulfinate **5a** under the given experimental conditions. In order to elucidate the source of hydrogens in products **9a** and **10a** as well as the possible reaction pathway, the salt **2f** was treated with an excess of anhydrous sulfinate **5a'** in the presence of D₂O (run 7). Proton NMR monitoring of the product mixture clearly revealed that deuterium was quantitatively incorporated into the *cis* position of the sulfone **9b** and the *trans* position of the bis(sulfone) **10b**. This finding suggests that the Michael addition of sulfinate **5** would compete with the ligand coupling in the intermediary species **14**; in the presence of excess of the sulfinate, the resulting ylide **15** would be readily protonated to form unstable alkylbismuthonium ion **16** as an intermediate. β -Elimination of the bismuthane moiety from compound **16** leads to sulfone **9**, while the S_N2-type displacement by sulfinate ion gives bis(sulfone) **10**.

Treatment of salts **2** with sodium thiolate **11** gave two sulfides

[‡] Prop-1-enyl(phenyl)iodonium salt is known to react with sulfinate to form a similar type of product.⁶

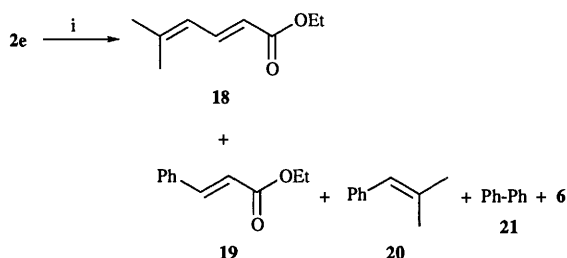


Scheme 3 Reagents: i, TolSO₂Na; ii, D₂O; iii, OH⁻; iv, TolSO₂⁻

12 and **13** (Scheme 2). It is noteworthy that an orange colour developed immediately after mixing of the components at low temperature and it gradually faded away as the reaction proceeded. A similar phenomenon was observed for the reaction of 2-oxoalkylbismuthonium salts with thiolate.² Although no spectroscopic evidence is available at present, it is highly likely that a bismuth(v) compound having four Bi–C bonds and one Bi–S bond is generated at low temperature and undergoes ligand coupling between the sulfur and carbon atoms to yield the expected sulfides.

Pd-catalysed reaction of alkenylbismuthonium salt **2e** with ethyl acrylate **17**

It is known that arylbismuth(III) and -(V) compounds undergo the Heck arylation in the presence of a palladium catalyst.^{7,8} Alkenylbismuthonium salt **2e** was found to undergo a similar type of reaction. In the presence of a catalytic amount of palladium diacetate or palladium tetrakis(triphenylphosphane), the salt **2e** reacted with ethyl acrylate **17** to give several coupling products (Scheme 4). The dienolate **18** and cinnamate **19** were the products arising from the Heck vinylation and arylation, whereas 2-methyl-1-phenylpropene **20** and biphenyl **21** were the products from the coupling between the bismuth-derived organyl ligands.⁹ Although the yield and selectivity of the

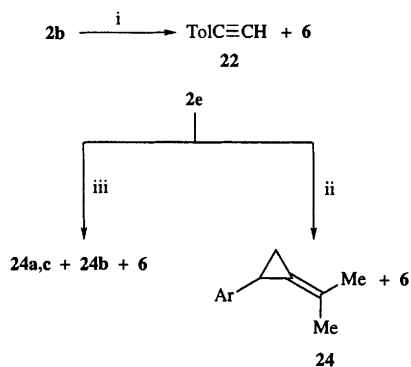


Scheme 4 Reagents and conditions: i, Pd(OAc)₂ or Pd(PPh₃)₄ (0.02–0.1 mol equiv.), ethyl acrylate **17** (2.5 mol equiv.), NaHCO₃ or NEt₃ (5 mol equiv.), DMF, room temp., 1.5–12 h

products were unsatisfactory, this result confirmed that all organyl ligands in alkenylbismuthonium salts can undergo smooth oxidative addition to a palladium complex to form reactive organopalladium species.

Reaction of alkenylbismuthonium salts **2** with a base

We have recently reported that treatment with an appropriate base removes the α -proton from 2-oxoalkylbismuthonium salts to generate the corresponding bismuthonium ylides, which are characterized by their unique reactivities arising from the high leaving ability of the triphenylbismuthonio moiety.^{10,11} Since the alkenylbismuthonium salts **2** also possess an acidic α -proton, it is expected that the base-promoted α -elimination would give rise to an alkylidene carbene or a carbenoid as a reactive species. Reaction of salt **2b** with KOBu^t afforded *p*-tolylacetylene **22** in moderate yield together with the bismuthane **6** (Scheme 5). This result can be well understood by assuming the instantaneous 1,2-hydrogen migration of the alkylidene carbene generated from salt **2b**. When treated with KOBu^t in the presence of excess of styrene derivatives **23**, the salt **2e** gave cyclopropanes **24** in high yields with quantitative recovery of bismuthane **6** (Scheme 5). In order to get better



Scheme 5 Reagents and conditions: i, KOBu^t, CH₂Cl₂, –78 °C to room temp.; ii, KOBu^t, ArCH=CH₂ **23** (a; Ar = 4-MeC₆H₄; b; Ar = Ph; c; Ar = 4-ClC₆H₄) (20 mol equiv.), CH₂Cl₂, –78 °C to room temp.; iii, KOBu^t, **23b** (20 mol equiv.), **23a** or **23c** (20 mol equiv.), CH₂Cl₂, –78 °C to room temp.

sight into the nature of the carbene or carbenoid intermediate, a Hammett study was made for this cyclopropanation.¹¹ The relative reactivity of the styrene derivatives **23a–c** was determined by treating salt **2e** with a base in the presence of a large excess of an equimolar mixture of two styrene derivatives. As is apparent from Table 4, the more electron-rich styrene was preferentially converted to the cyclopropane **24**. The ρ -values for some typical cyclopropanations are summarized in Table 5. It is generally accepted that alkylidene carbenes are moderately electrophilic and show relatively small negative ρ -values, whilst carbenoids are considerably electrophilic and show larger negative ρ -values.¹² Thus, comparison of the present ρ -value with those reported for related cyclopropanations has revealed that the alkylidene species generated from bismuthonium salt **2e**

Table 4 Yield of cyclopropanes **24** and relative reactivity of styrenes **23a–c**

Run	Styrene 23	Product 24 (%) ^a	k_{rel} ^b
1	23a (R = Me)	24a (93)	1.16
2	23b (R = H)	24b (84)	1.00
3	23c (R = Cl)	24c (86)	0.86

^a Numeral in parenthesis refers to GLC yield of a product **24** obtained in the reaction of salt **2e** with 20 mol equiv. of corresponding styrene **23**.

^b Relative reactivity *vs* styrene **23b** determined by competitive method.

possesses a free carbene character close to those derived from the iodonium salt, vinyl triflate and vinyl diazomethane, in accordance with the high leaving ability of the bismuthonio group as a bismuthane.

Further study on the synthesis and reactions of different types of functionalized alkylbismuthonium compounds is in progress.

Experimental

All reactions with air-sensitive compounds were carried out under argon. Dichloromethane (CH₂Cl₂) and tetrahydrofuran (THF) were distilled under argon from CaH₂ and sodium benzophenone ketyl, respectively, before use. DMF was distilled from CaH₂ and stored over molecular sieves 4 Å. Triphenylbismuth difluoride,¹⁷ alkenyl-silanes **1**¹⁸ and -stannanes **3**¹⁹ were prepared according to the reported procedures. Ethyl acrylate **17**, styrene and its derivatives **23** were all commercial products and purified by distillation before use. Other reagents were used as commercially received. Column chromatography was performed on silica gel (Wakogel, 200 mesh). All mps were determined on a Yanagimoto hot-stage apparatus and are uncorrected. ¹H (200 MHz) and ¹³C (50 MHz) NMR were recorded on a Varian Gemini-200 spectrometer for solutions in CDCl₃ unless otherwise stated, with tetramethylsilane as internal standard. Coupling constants *J* are given in Hz. IR spectra were observed on a Shimadzu FTIR-8100S spectrophotometer. EI mass spectra were obtained on a Shimadzu GCMS-QP2000A spectrometer and FAB mass spectra on a JEOL JMS-HS110 spectrometer using 3-nitrobenzyl alcohol as matrix. GLC analysis was carried out on a Shimadzu GC-14A gas chromatograph, using a CBP-1-M25-025 column [25 m × 0.2 mm (i.d.)] with cyclododecane as the internal standard for quantitative determination. Elemental analyses were performed at the Microanalytical Laboratory of Kyoto University.

Synthesis of alkenyltriphenylbismuthonium salts **2**

From the silanes 1. To an ice-cooled CH₂Cl₂ (5 cm³) solution of triphenylbismuth difluoride (478 mg, 1 mmol) were added successively BF₃·OEt₂ (0.13 cm³, 1 mmol) and alkenyltrimethylsilane **1** (1 mmol). The resulting mixture was heated under gentle reflux for 12–25 h to complete the reaction. Evaporation off of the solvent under reduced pressure left an oily residue, which was washed with hexane (5 cm³ × 2) and then was fractionally crystallized from Et₂O–CH₂Cl₂ (1:1) to afford small amounts of tetraphenylbismuthonium tetrafluoroborate as a crystalline solid. The mother liquid was concentrated and passed through a short silica gel column, using CH₂Cl₂ as the eluent, to afford alkenyltriphenylbismuthonium tetrafluoroborate **2** in the yields listed in Table 1.

From the stannanes 3. To an ice-cooled CH₂Cl₂ (5 cm³) solution of triphenylbismuth difluoride (478 mg, 1 mmol) were added successively BF₃·OEt₂ (0.13 cm³, 1 mmol) and Me₃SiCN (0.13 cm³, 1 mmol). After 2 h, alkenylstannane **3** (1 mmol) was added and the resulting mixture was stirred for an additional 12 h at room temperature to complete the reaction. Evaporation of the mixture under reduced pressure left an oily residue,

Table 5 ρ -Values for the reaction of 2-methylprop-1-enylidene with styrenes

Entry	Carbene precursor	Reaction conditions	ρ
1	2e	KOBu ^t /CH ₂ Cl ₂ /-78 °C to room temp.	-0.33 (σ)
2	[PhI ⁺ CH=CMe ₂]BF ₄ ⁻	KOBu ^t /CH ₂ Cl ₂ /3 °C	-0.55 (σ) ¹³
3	Me ₂ C=CN ₂	KOBu ^t /CH ₂ Cl ₂ /-78 °C	-0.51 (σ) ¹⁴
4	Me ₂ C=CHOTf	KOBu ^t /-20 °C	-0.75 (σ) ¹⁵
5	Me ₂ C=CHBr	KOBu ^t /-10 °C	-4.2 (σ^+) ¹⁶
6	Me ₂ C=CBr ₂	MeLi/-40 °C	-4.3 (σ^+) ¹⁶

which was passed through a short silica gel column with CH₂Cl₂ as the eluent. The eluate was evaporated under reduced pressure to leave an oily residue, which was crystallized from Et₂O-CH₂Cl₂ (10:1) to afford alkenyltriphenylbismuthonium tetrafluoroborate **2** in the yields listed in Table 1.

(E)-2-Phenylethenyl(triphenyl)bismuthonium tetrafluoroborate 2a. Glass; δ_{H} 7.30 (1 H, d, *J* 17.0), 7.34–7.36 (3 H, m), 7.54–7.66 (12 H, m) and 7.75 (6 H, d, *J* 7.5); δ_{C} 125.3, 127.9, 129.1, 130.7, 132.2, 132.3, 135.3, 135.8, 137.3 and 151.7; ν_{max} (KBr)/cm⁻¹ 1565, 1476, 1437, 1150–950, 727 and 685; *m/z* (FAB) 543 (M⁺ – BF₄), 389, 363, 286 and 209 (Found: C, 49.7; H, 3.55. C₂₆H₂₂BBiF₄ requires C, 49.55; H, 3.5%).

(E)-2-(4-Methylphenyl)ethenyl(triphenyl)bismuthonium tetrafluoroborate 2b. Glass; δ_{H} 2.36 (3 H, s), 7.18 (2 H, d, *J* 8.1), 7.25 (1 H, d, *J* 16.5), 7.44 (2 H, d, *J* 8.1) and 7.55–7.88 (16 H, m); δ_{C} 22.7, 125.1, 129.1, 131.0, 133.3, 133.4, 133.8, 137.0, 138.5, 142.5 and 152.8; ν_{max} (KBr)/cm⁻¹ 1509, 1474, 1285, 1200–900, 992, 729, 685 and 650; *m/z* (FAB) 557 (M⁺ – BF₄), 363, 286 and 209 (Found: C, 50.15; H, 3.8. C₂₇H₂₄BBiF₄ requires C, 50.3; H, 3.75%).

(E,E)-4-Phenylbuta-1,3-dienyl(triphenyl)bismuthonium tetrafluoroborate 2c. Glass; δ_{H} 6.71 (1 H, d, *J* 14.7), 6.90–7.06 (1 H, m) and 7.27–7.85 (22 H, m); ν_{max} (KBr)/cm⁻¹ 1474, 1437, 1260, 1150–900, 995, 765, 729 and 685; *m/z* (FAB) 569 (M⁺ – BF₄), 363, 286 and 209 (Found: C, 50.7; H, 3.5. C₂₈H₂₄BBiF₄ requires C, 51.2; H, 3.7%).

(Z)-Oct-1-enyl(triphenyl)bismuthonium tetrafluoroborate 2d. Glass; δ_{H} 0.78 (3 H, t, *J* 7.3), 0.93–1.35 (8 H, m), 2.12 (2 H, q, *J* 7.5) and 7.50–7.85 (17 H, m); δ_{C} 13.9, 22.4, 28.5, 28.7, 31.3, 37.8, 126.3, 132.1, 132.2, 135.6, 137.7 and 152.4; ν_{max} (neat)/cm⁻¹ 3000–2800, 1566, 1476, 1437, 1285, 1150–950, 992, 733 and 687; *m/z* (FAB) 551 (M⁺ – BF₄), 397, 363, 286 and 209 (Found: C, 48.3; H, 4.5. C₂₆H₃₀BBiF₄ requires C, 48.9; H, 4.7%).

2-Methylprop-1-enyl(triphenyl)bismuthonium tetrafluoroborate 2e. Mp 147–148 °C; δ_{H} 1.94 (3 H, s), 2.26 (3 H, d, *J* 1.3) and 7.55–7.81 (16 H, m); δ_{C} 27.5 (two methyl carbons), 118.9, 132.2, 132.3, 135.5, 136.6 and 160.0; ν_{max} (KBr)/cm⁻¹ 1609, 1566, 1476, 1435, 1256, 1150–1000, 745, 723 and 683; *m/z* (FAB) 495 (M⁺ – BF₄), 286 and 209 (Found: C, 45.4; H, 3.8. C₂₂H₂₂BBiF₄ requires C, 45.4; H, 3.8%).

(E)-Prop-1-enyl(triphenyl)bismuthonium tetrafluoroborate 2f. Mp 110–111 °C; δ_{H} 2.10 (3 H, dd, *J* 6.5 and 1.4), 6.59 (1 H, dd, *J* 15.4 and 6.5) and 7.50–7.85 (16 H, m); δ_{C} 22.6, 124.9, 132.1, 132.2, 135.8, 136.8 and 152.3; ν_{max} (KBr)/cm⁻¹ 1566, 1474, 1435, 1150–950, 735 and 689; *m/z* (FAB) 481 (M⁺ – BF₄), 363, 327, 286, 250 and 209 (Found: C, 44.4; H, 3.5. C₂₁H₂₀BBiF₄ requires C, 44.4; H, 3.55%). As for *E/Z* mixture **2f**, the *E/Z* ratio was estimated by ¹H NMR spectroscopy.

Reaction of salt **2** with hydrated sodium sulfinate **5**

Typical procedure. A mixture of salt **2e** (291 mg, 0.50 mmol), sodium toluene-*p*-sulfinate tetrahydrate **5a** (1.25 g, 5.0 mmol) and DMF (5 cm³) was stirred at room temperature for 12 h and then diluted with water (20 cm³). The organic layer was extracted with Et₂O (10 cm³ × 3) and the combined extracts were washed with brine (10 cm³ × 2), dried (Na₂SO₄), and concentrated under reduced pressure to leave an oily residue, which was chromatographed on silica gel using hexane-ethyl acetate (10:0–8:2) as the eluent to give triphenylbismuthane **6**

(163 mg, 74%), sulfone **7d** (45 mg, 43%) and phenyl *p*-tolyl sulfone **8** (10 mg, 9%). The products were identified by comparison with authentic specimens.

(E)-4-Methylphenyl 2-phenylethenyl sulfone 7a. Mp 121–122 °C (lit.,²⁰ 120–121 °C); δ_{H} 2.44 (3 H, s), 6.85 (1 H, d, *J* 15.4), 7.31–7.50 (7 H, m), 7.66 (1 H, d, *J* 15.4) and 7.83 (2 H, d, *J* 8.3); ν_{max} (KBr)/cm⁻¹ 1595, 1451, 1316, 1304, 1285, 1144, 1086, 974, 860, 810, 749 and 666; *m/z* (EI) 258 (M⁺), 193, 139, 119, 103, 91 and 77 (Found: C, 69.5; H, 5.5. Calc. for C₁₅H₁₄O₂S: C, 69.7; H, 5.5%).

(E)-2-(4-Methylphenyl)ethenyl phenyl sulfone 7b. Mp 138–139 °C (lit.,²¹ 140.5–141.0 °C); δ_{H} 2.36 (3 H, s), 6.81 (1 H, d, *J* 15.5), 7.19 (2 H, d, *J* 8.1), 7.38 (2 H, d, *J* 8.1), 7.45–7.60 (3 H, m), 7.66 (1 H, d, *J* 15.5) and 7.94 (2 H, m); ν_{max} (KBr)/cm⁻¹ 1605, 1449, 1308, 1148, 1084, 974, 866, 831, 787, 752, 731 and 685; *m/z* (EI) 258 (M⁺), 149, 125, 116, 105, 97 and 77.

(E,E)-Phenyl 4-phenylbuta-1,3-dienyl sulfone 7c.²² Mp 91–92 °C; δ_{H} 6.45 (1 H, d, *J* 14.7), 6.77 (1 H, dd, *J* 15.5 and 10.4), 7.01 (1 H, d, *J* 15.5), 7.30–7.65 (9 H, m) and 7.92 (2 H, m); ν_{max} (KBr)/cm⁻¹ 1586, 1447, 1308, 1140, 1084, 997, 818, 787, 754 and 687; *m/z* (EI) 270 (M⁺), 126, 117, 115 and 77 (Found: C, 71.1; H, 5.2. C₁₆H₁₄O₂S requires C, 71.1; H, 5.2%).

4-Methylphenyl 2-methylprop-1-enyl sulfone 7d. Oil (lit.,²⁰ mp 62–63 °C); δ_{H} 1.87 (3 H, d, *J* 1.3), 2.14 (3 H, d, *J* 1.3), 2.43 (3 H, s), 6.17 (1 H, sept, *J* 1.3), 7.32 (2 H, d, *J* 8.4) and 7.78 (2 H, d, *J* 8.4); *m/z* (EI) 210 (M⁺), 193, 155, 139 and 91.

(E)-4-Methylphenyl prop-1-enyl sulfone 7e.²³ δ_{H} 1.91 (3 H, dd, *J* 6.9 and 1.6), 2.44 (3 H, s), 6.33 (1 H, dq, *J* 15.0 and 1.6), 6.95 (1 H, dq, *J* 15.0 and 6.9), 7.33 (2 H, d, *J* 8.2) and 7.76 (2 H, d, *J* 8.2).

1-Methylethenyl 4-methylphenyl sulfone 9a.²⁴ δ_{H} 1.95 (3 H, d, *J* 0.8), 2.44 (3 H, s), 5.68 (1 H, m), 6.25 (1 H, s), 7.34 (2 H, d, *J* 8.0) and 7.77 (2 H, d, *J* 8.5).

1,2-Bis(4-methylphenylsulfonyl)propane 10a. Mp 143–144 °C (lit.,⁶ 142–143 °C); δ_{H} 1.49 (3 H, d, *J* 6.8), 2.47 (6 H, s), 3.11 (1 H, dd, *J* 13.7 and 11.0), 3.45–3.60 (1 H, m), 3.74 (1 H, dd, *J* 13.7 and 1.5), 7.36 (4 H, d, *J* 8.3), 7.68 (2 H, d, *J* 8.3) and 7.74 (2 H, d, *J* 8.3).

Reaction of salt **2f** with anhydrous sodium sulfinate **5a'** in the presence of D₂O

To a stirred solution of anhydrous sodium toluene-*p*-sulfinate **5a'** (267 mg, 1.5 mmol) in DMF (1.5 cm³)-D₂O (0.11 cm³, 6.0 mmol) was added salt **2f** (85 mg, 0.15 mmol) at room temperature. After being stirred for 12 h, the mixture was diluted with water (10 cm³), and the organic layer was extracted with Et₂O (10 cm³ × 3). The combined extracts were washed with water (10 cm³ × 2), dried (MgSO₄) and concentrated under reduced pressure to leave an oily residue, which was chromatographed as described above to give triphenylbismuthane **6** (61 mg, 92%), sulfones **7e** (2.6 mg, 9%), **8** (1.5 mg, 4%) and **9b** (7.1 mg, 24%), and bis-sulfone **10b** (10.9 mg, 21%). The stereoisomers of compounds **9b** and **10b** were not detected in the NMR spectra.

(Z)-2-Deuterio-1-methylethenyl 4-methylphenyl sulfone 9b. δ_{H} 1.95 (3 H, d, *J* 1.5), 2.45 (3 H, s), 5.67 (1 H, q, *J* 1.5), 7.34 (2 H, d, *J* 8.4) and 7.77 (2 H, d, *J* 8.4).

(1R*,2S*)-1-Deuterio-1,2-bis(4-methylphenylsulfonyl)propane 10b. δ_{H} 1.49 (3 H, d, *J* 6.8), 2.47 (6 H, s), 3.10 (1 H, d, *J*

11.3), 3.52 (1 H, dq, J 11.3 and 6.8), 7.37 (4 H, d, J 8.4), 7.69 (2 H, d, J 8.4) and 7.75 (2 H, d, J 8.4).

Reaction of salts **2** with sodium benzenethiolate **14**

Typical procedure. To a solution of sodium benzenethiolate **14** prepared from NaH (40 mg; 60% oil dispersion; 1 mmol) and benzenethiol (0.1 cm³, 1 mmol) in THF (5 cm³) was added salt **2e** (581 mg, 1 mmol) at -50°C . The reaction mixture was gradually warmed to room temperature and filtered through a Celite bed. The filtrate was concentrated under reduced pressure to leave an oily residue, which was chromatographed as described above to give triphenylbismuthane **6** (207 mg, 47%), sulfide **12a** (53 mg, 32%) and diphenyl sulfide **13** (54 mg, 29%). The products were identified by comparison with authentic specimens.

2-Methylprop-1-enyl phenyl sulfide 12a. Oil (lit.,²⁵ bp 111–112 $^{\circ}\text{C}/9$ mmHg); δ_{H} 1.87 (3 H, d, J 1.3), 1.89 (3 H, d, J 1.3), 5.91 (1 H, sept, J 1.3) and 7.10–7.30 (5 H, m); m/z (EI) 164 (M^+), 149 and 109.

(E)-Phenyl prop-1-enyl sulfide 12b.²⁶ Oil; δ_{H} 1.84 (3 H, dd, J 6.2 and 1.1), 5.75–6.25 (2 H, m) and 7.15–7.37 (5 H, m).

Heck-type reaction of salt **2e** with ethyl acrylate **17**

Typical procedure. A mixture of salt **2e** (291 mg, 0.50 mmol), ethyl acrylate **17** (250 mg, 2.5 mmol), sodium carbonate (420 mg, 5.0 mmol), Pd(OAc)₂ (2.2 mg, 0.01 mmol) and DMF (2 cm³) was stirred at room temperature. After 1.5 h, saturated aq. NH₄Cl (10 cm³) was added and the organic layer was extracted with ethyl acetate (10 cm³ \times 3). The combined extracts were washed successively with water (10 cm³) and brine (10 cm³), dried (MgSO₄), and evaporated under reduced pressure to leave an oily residue, which was chromatographed as described above to elute 2-methyl-1-phenylpropene **20** (12 mg, 19%), biphenyl **21** (10 mg, 13%), the bismuthane **6** (92 mg, 42%), ethyl 5-methylhexa-2,4-dienoate **18** (15 mg, 19%) and ethyl cinnamate **19** (11 mg, 13%) in this order. The yields were based on salt **2e** used. Since the last two products were inseparable, their relative ratio was estimated by ¹H NMR and GC analyses. Compound **18** was identified by direct comparison with an authentic specimen.²⁷ When 0.05 mmol of Pd(OAc)₂ was used, the yields of compounds **18** and **19** were 29 and 27%, respectively. When a combination of Pd(PPh₃)₄ (58 mg, 0.05 mmol) and triethylamine (505 mg, 5.0 mmol) was used as the catalyst, the respective yields of the products **20**, **21**, **6**, **18** and **19** were 20, 77, 11, 15 and 9% based on salt **2e** used.

Reaction of salt **2b** with KOBu^t

To a solution of salt **2b** (127 mg, 0.20 mmol) in CH₂Cl₂ (3 cm³) was added KOBu^t (23 mg, 0.20 mmol) at -78°C and the resulting mixture was allowed gradually to warm to room temperature. The mixture was passed through a short silica gel column, using CH₂Cl₂ as the eluent, to give bismuthane **6** (80 mg, 91%) and 4-methylphenylacetylene **22** (15 mg, 65%).

Reaction of salt **2e** with KOBu^t in the presence of styrenes **23**

To a mixture of salt **2e** (175 mg, 0.30 mmol), a styrene **23a–c** (6 mmol) and CH₂Cl₂ (3 cm³) was added KOBu^t (34 mg, 0.30 mmol) at -78°C . The resulting mixture was allowed gradually to warm to room temperature and was passed through a short silica gel column, using CH₂Cl₂ as the eluent, to give bismuthane **6**, unreacted styrene **23a–c** and the corresponding cyclopropane **24**. The yields of products were determined by ¹H NMR and GLC analysis. The cyclopropanes **24** were identified by direct comparison with authentic specimens.

Compound **24a**.¹² δ_{H} (for aliphatic protons) 1.03 (1 H, m), 1.61 (1 H, m), 1.78 (3 H, m), 1.89 (3 H, m) and 2.53 (1 H, m).

Compound **24b**.²⁸ δ_{H} (for aliphatic protons) 1.06 (1 H, m), 1.66 (1 H, m), 1.73 (3 H, m), 1.91 (3 H, m) and 2.57 (1 H, m).

Compound **24c**.¹² δ_{H} (for aliphatic protons) 1.04 (1 H, m), 1.66 (1 H, m), 1.76 (3 H, m), 1.90 (3 H, m) and 2.51 (1 H, m).

Competitive reaction of styrenes **23a–c** with salt **2e** in the presence of KOBu^t

To a stirred mixture of salt **2e** (58 mg, 0.1 mmol), styrene **23b** (2 mmol), a substituted styrene **23a,c** (2 mmol) and CH₂Cl₂ (1 cm³) was added KOBu^t (12 mg, 0.1 mmol) at -78°C , and the resulting mixture was allowed to warm to room temperature. The mixture was passed through a short silica gel column, using CH₂Cl₂ as the eluent, to give a mixture of cyclopropanes **24** and unreacted styrenes **23**, the yields of which were determined by ¹H NMR and GLC analysis.

X-Ray crystallography of compound **2e**

A crystal of dimensions 0.330 \times 0.230 \times 0.080 mm, grown from Et₂O–CH₂Cl₂ (2:1), was coated with manicure wax to avoid damage from air and moisture.

Crystal data. C₂₂H₂₂BBiF₄, $M = 582.20$. Monoclinic. Space group $P2_1/n$, $a = 10.448(2)$, $b = 18.166(4)$, $c = 11.420(1)$ Å, $\beta = 91.85(1)^{\circ}$, $V = 2166.2(6)$ Å³ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections in the range $20.02 < 2\theta < 22.03^{\circ}$, 298 K, Mo–K α radiation, $\lambda = 0.71069$ Å), $Z = 4$, $D_c = 1.785$ g cm⁻³. Plate, $\mu(\text{Mo–K}\alpha, \lambda = 0.71069 \text{ \AA}) = 81.8$ cm⁻¹, $F(000) = 1112$.

Data collection and processing. Intensity data were collected on a Rigaku AFC5R diffractometer using graphite-monochromated Mo–K α radiation from a fine-focus anode of the 12 kW type rotating anode generator with the ω – 2θ scan technique to a maximum 2θ -value of 55.0° . Data were corrected for Lorentz and polarization effects. The intensities of three representative reflections which were measured after every 150 reflections declined by (–) 7.20%. A linear correction factor was applied to the data to account for this phenomenon. An empirical absorption correction, based on azimuthal scans of five reflections, was applied which resulted in transmission factors ranging from 0.38 to 1.00. Scans of $(0.84 + 0.30 \tan \theta)^{\circ}$ were made at a speed of $16.0^{\circ} \text{ min}^{-1}$ (in ω). Of the 5391 reflections which were collected, 5125 were unique ($R_{\text{int}} = 0.037$).

Structure analysis and refinement. The structure was solved by a combination of the Patterson method and direct methods.²⁹ The non-hydrogen atoms were refined anisotropically. The parameters of hydrogen atoms were idealized [$\text{C–H } 0.95 \text{ \AA}$, $B(\text{H}) = 1.2B_{\text{eq}}(\text{C})$]. The final cycle of full-matrix least-squares refinement was based on 2735 observed reflections [$I > 3.00\sigma(I)$] and 254 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.036$ and $R_w = 0.033$. The weighting scheme, $w = 1/\sigma^2(F_o)$, was employed. Neutral atom-scattering factors were taken from Cromer and Waber.³⁰ Anomalous dispersion effects were included in F_{calc} .³¹ The values for $\Delta f'$ and $\Delta f''$ were those of Cromer.³² All calculations were performed using the TEXSAN³³ crystallographic software package of the Molecular Structure Corporation. The ORTEP³⁴ program was used to obtain Fig. 1. Selected bond lengths and bond angles are given in Table 2.§

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§ Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/26.

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