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Journal of Organometallic Chemistry 611 (2000) 89–99

Journal of Organometallic Chemistry

Stabilized bismuthonium ylides bearing a highly cross-conjugated ylidic carbon atom: synthesis, structures, and reactions

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Received 1 March 2000; accepted 15 March 2000

Abstract

The reaction of iminotriaryl-λ^5-bismuthanes (**2**; $Ar_3Bi{=}NR$; $R = COR''$ or SO_2R'') with dialkyl acetylenedicarboxylates (**3**; $R'O_2CC{\equiv}CCO_2R'$) has been found to afford highly stabilized bismuthonium ylides (**4**; $Ar_3Bi{=}C(CO_2R')–C(CO_2R'){=}NR$) in 50–92% yield. The X-ray crystallographic analyses of two of these ylides demonstrated that their bismuth center possesses a distorted tetrahedral geometry with the highly cross-conjugated ylidic carbon atom. The observed Bi–C_{ylide} bond lengths of 2.178(7)–2.199(7) Å are close to ordinary Bi–C_{Ar} bond lengths, suggesting an appreciable single bond character of the Bi–C_{ylide} bond. The action of two equivalents of acetic acid, hydrogen chloride, or 4-nitrophenol on **4** cleaved the Bi–C_{ylide} bond to give the corresponding triarylbismuth(V) compounds of the type Ar_3BiX_2 and olefins (**5**; $R'O_2CCH{=}C(CO_2R')NHR$). 4-Nitrobenzenethiol was oxidized by 0.5 equivalents of **4** to give bis(4-nitrophenyl) disulfide with a good recovery of triarylbismuthane **6** and olefin **5**. On thermolysis at 200°C, or when decomposed in the presence of a copper catalyst at room temperature, the ylides **4** bearing an *N*-aroyl group gave 2,4,5-trisubstituted oxazoles **7** and triarylbismuthanes **6** in moderate to excellent yields. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Iminotriaryl-λ^5-bismuthanes; Bismuthonium ylides; Acetylenes; X-ray crystallographic analysis; Copper catalyst; Oxazoles

1. Introduction

Bismuthonium ylides constitute a class of organobismuth compounds bearing a formal double bond between the bismuth(V) and carbon atoms [1]. Most of the known bismuthonium ylides bear carbonyl or sulfonyl groups on the ylidic carbon and are divided into two types; the α,α-dicarbonyl or α,α-disulfonyl type ($Ph_3Bi{=}CX_2$; $X = COR$ or SO_2R) [2] and the α-monocarbonyl type ($Ph_3Bi{=}CHCOR$) [3]. The former type of bismuthonium ylides is thermally stable; compound **1** undergoes a Wittig-type olefination with aldehydes at 40–80°C [4]. In contrast, the latter type of bismuthonium ylides is thermally unstable and readily undergoes a Corey–Chaycovsky-type epoxide formation with aldehydes at low temperatures [3]. Thus, the stability and reactivity of bismuthonium ylides vary considerably depending on the electronic environment around the ylidic carbon atom. The reaction modes of these bismuthonium ylides contrast to those observed for the analogous ylides derived from lighter pnictogen elements [5].

However, the number of well-characterized bismuthonium ylides is still limited, and the literature to date includes only one example of X-ray structure analysis [6]. To get better insight into this class of compounds, it is necessary to prepare a different type of bismuthonium ylide and to disclose its properties and reactivity. Until now, there have been three known methods available for the synthesis of bismuthonium ylides, which include the metathesis between Ar_3BiX_2 ($X_2 = Cl_2$, O, CO_3) and 1,3-dicarbonyl or 1,3-disulfonyl compounds [2b–e], the carbene-transfer from diazo compounds to triphenylbismuthane [2a,7], and the α-proton abstraction by a base from 2-oxoalkylbismuthonium salts [3]. In this paper, we report an additional new method for the synthesis of stabilized bismuthonium ylides bearing a highly cross-conjugated ylidic

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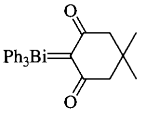
PII: S0022-328X(00)00295-3

carbon atom, exploiting the reaction between iminotriaryl-λ^5-bismuthanes and dialkyl acetylenedicarboxylates. The X-ray structures and some reactions of the novel bismuthonium ylides obtained are also presented.



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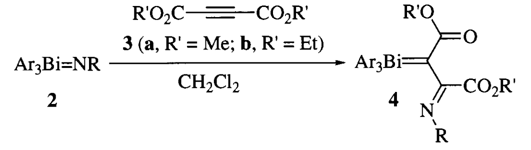
2. Results and discussion

2.1. Synthesis of compounds **4**

As shown in Scheme 1, (acylimino)triaryl-λ^5-bismuthanes [8] **2a**–**g** reacted with dimethyl acetylenedicarboxylate (**3a**) to afford bismuthonium ylides **4a**–**g** in 57–92% yield (entries 1–7 in Table 1). When phenylacetylene, diphenylacetylene, or ethyl 2-butynoate was used instead of **3a**, no coupling reaction took place. (Sulfonylimino)triaryl-λ^5-bismuthanes **2h**–**j** similarly reacted with **3a** and **3b**, albeit slowly, to afford the corresponding bismuthonium ylides **4h**–**m** in 50–70% yield (entries 8–13). Imino-λ^5-bismuthanes **2c**,**e**,**f**,**g**,**i**,**j** were prepared from the corresponding triarylbismuth dichlorides and amides according to Eq. (1) and used without isolation for the subsequent reactions.

$$Ar_3BiCl_2 + H_2NR \xrightarrow[CH_2Cl_2,\ -50\ °C\ to\ r.t.]{KO\text{-}t\text{-}Bu\ (2\ equiv)} \underset{\mathbf{2c,f,g,i,j}}{Ar_3Bi{=}NR} \qquad (1)$$

The ylides **4** were purified by column chromatography on silica gel followed by recrystallization from



2a; Ar = *o*-Tol, R = COCF$_3$
2b; Ar = *o*-Tol, R = COC$_6$H$_3$-3,5-(CF$_3$)$_2$
2c; Ar = *o*-Tol, R = COC$_6$H$_4$-4-NO$_2$
2d; Ar = *o*-Ans, R = COCF$_3$
2e; Ar = *o*-Ans, R = COC$_6$H$_3$-3,5-(CF$_3$)$_2$
2f; Ar = *o*-Ans, R = COC$_6$H$_4$-4-NO$_2$
2g; Ar = *o*-Ans, R = COC$_6$H$_4$-4-CN
2h; Ar = *p*-Tol, R = SO$_2$CF$_3$
2i; Ar = *p*-Tol, R = SO$_2$Ph
2j; Ar = Ph, R = SO$_2$Tol-*p*

4a; Ar = *o*-Tol, R = COCF$_3$, R' = Me
4b; Ar = *o*-Tol, R = COC$_6$H$_3$-3,5-(CF$_3$)$_2$, R' = Me
4c; Ar = *o*-Tol, R = COC$_6$H$_4$-4-NO$_2$, R' = Me
4d; Ar = *o*-Ans, R = COCF$_3$, R' = Me
4e; Ar = *o*-Ans, R = COC$_6$H$_3$-3,5-(CF$_3$)$_2$, R' = Me
4f; Ar = *o*-Ans, R = COC$_6$H$_4$-4-NO$_2$, R' = Me
4g; Ar = *o*-Ans, R = COC$_6$H$_4$-4-CN, R' = Me
4h; Ar = *p*-Tol, R = SO$_2$CF$_3$, R' = Me
4i; Ar = *p*-Tol, R = SO$_2$Ph, R' = Me
4j; Ar = Ph, R = SO$_2$Tol-*p*, R' = Me
4k; Ar = *p*-Tol, R = SO$_2$CF$_3$, R' = Et
4l; Ar = *p*-Tol, R = SO$_2$Ph, R' = Et
4m; Ar = Ph, R = SO$_2$Tol-*p*, R' = Et

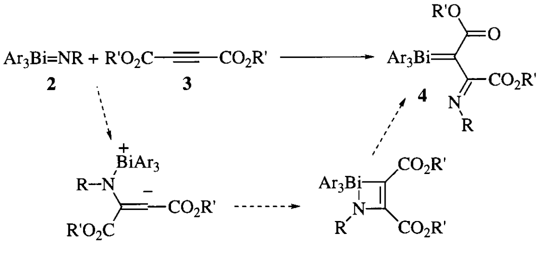
Scheme 1.

Table 1
Synthesis of bismuthonium ylides **4**

Entry	**2**	**3** (equivalents)	Solvent	Conditions	Ylide **4**	Yield (%) [a]
1	**2a**	**3a** (3)	C_6H_6	60°C, 15 h	**4a**	82
2	**2b**	**3a** (5)	CH_2Cl_2	r.t., 15 h	**4b**	75
3	**2c**	**3a** (5)	CH_2Cl_2	r.t., 15 h	**4c**	59 [b]
4	**2d**	**3a** (3)	C_6H_6	60°C, 15 h	**4d**	72
5	**2e**	**3a** (3)	CH_2Cl_2	r.t., 20 h	**4e**	92 [b]
6	**2f**	**3a** (3)	CH_2Cl_2	r.t., 10 h	**4f**	59 [b]
7	**2g**	**3a** (3)	CH_2Cl_2	r.t., 24 h	**4g**	57 [b]
8	**2h**	**3a** (2)	CH_2Cl_2	40°C, 20 h	**4h**	70
9	**2i**	**3a** (2)	CH_2Cl_2	r.t., 74 h	**4i**	66 [b]
10	**2j**	**3a** (2)	CH_2Cl_2	r.t., 65 h	**4j**	51
11	**2h**	**3b** (2)	CH_2Cl_2	40°C, 24 h	**4k**	66
12	**2i**	**3b** (2)	CH_2Cl_2	r.t., 65 h	**4l**	54 [b]
13	**2j**	**3b** (2)	CH_2Cl_2	r.t., 91 h	**4m**	50 [b]

[a] Isolated yields based on **2**.

[b] Isolated yield based on the triarylbismuth dichloride.



Scheme 2.

Table 2
Crystal data for **4a** and **4c**

	4a	**4c**
Formula	$C_{29}H_{27}BiF_3NO_5$	$C_{68}H_{62}Bi_2N_4O_{14}$
Formula weight	735.51	1577.22
Crystal dimensions (mm)	0.40 × 0.28 × 0.20	0.05 × 0.05 × 0.05
Crystal system	Monoclinic	Triclinic
a (Å)	11.557(5)	17.876(3)
b (Å)	15.218(4)	18.130(3)
c (Å)	16.622(4)	10.288(4)
α (°)		100.52(2)
β (°)	99.33(3)	95.27(2)
γ (°)		100.90(1)
V (Å^3)	2884(1)	3191(1)
μ(Mo–K$_\alpha$) (cm^{-1})	61.57	55.65
Space group	$P2_1/c$	$P\bar{1}$
Z value	4	2
D_{calc} (g cm^{-3})	1.693	1.641
No. of reflections collected	6940	15136
No. of unique reflections	6622	14663
R_{int}	0.025	0.038
No. of observations	4128 [$I > 2.00\sigma(I)$]	14663 [$I > -10.00\sigma(I)$]
No. of variables	353	793
R_1	0.039	0.038
R_w	0.052	0.117
Goodness-of-fit	1.08	0.95

Table 3
Selected bond lengths (Å) and angles (°) of **4a**

Bond lengths		Bond angles	
Bi–C(3)	2.199(7)	C(3)–Bi–C(9)	113.9(3)
Bi–C(9)	2.225(8)	C(3)–Bi–C(16)	110.1(3)
Bi–C(16)	2.223(7)	C(3)–Bi–C(23)	113.7(3)
Bi–C(23)	2.216(7)	C(9)–Bi–C(16)	105.7(3)
C(2)–C(3)	1.45(1)	C(9)–Bi–C(23)	105.1(3)
C(3)–C(4)	1.35(1)	C(16)–Bi–C(23)	108.0(3)
C(4)–C(5)	1.51(1)	Bi–C(3)–C(2)	124.1(6)
C(4)–N	1.358(9)	Bi–C(3)–C(4)	109.5(5)
C(7)–N	1.33(1)	C(2)–C(3)–C(4)	125.6(7)
C(2)–O(4)	1.217(10)	C(3)–C(4)–C(5)	120.4(7)
C(2)–O(5)	1.33(1)	C(3)–C(2)–O(4)	124.4(8)
C(5)–O(2)	1.194(9)	C(4)–C(5)–O(2)	121.9(8)
C(5)–O(3)	1.319(9)	C(3)–C(4)–N	117.7(7)
C(7)–O(1)	1.21(1)	C(4)–N–C(7)	119.5(7)
Bi···N	2.863(6)	N–C(7)–O(1)	132.3(9)

CH_2Cl_2/hexane or EtOAc/pentane. These products are pale yellow crystalline solids, soluble in $CHCl_3$, CH_2Cl_2, CH_3CN, EtOAc, and benzene. Although all the ylides **4** decomposed at temperatures close to their melting points, they remained unchanged over a month at room temperature. Compounds **4e** and **4i** did not show any sign of decomposition even after heating at 60°C in $CDCl_3$ for 1 week. Thus, the present ylides **4** may be regarded to be new members of the family of highly stabilized bismuthonium ylides.

A plausible reaction pathway for the formal nitrenoid transfer is depicted in Scheme 2. The imido nitrogen atom adds to an electron-deficient acetylenic carbon to form a dipolar intermediate, which undergoes the 1,3-migration of the triarylbismuthonio group via a four-membered cyclic species, leading to the Bi=C–C=N structure of the final product **4**. A similar type of transformation has previously been reported for *N*-aryliminophosphoranes [9], but no reaction took place between an *N*-acyliminophosphorane $Ph_3P{=}NCOCF_3$ and acetylene **3a** at 40°C. Kuplennik et al. reported the formation of cyclic Sb(V) compounds containing an azastibetine structure from the reaction of (sulfonylimino)triaryl-λ^5-stibanes, $Ar_3Sb{=}NSO_2Ph$ (Ar = Ph, *p*-Tol), and **3b** on the basis of NMR and IR spectroscopy [10].

2.2. Structures of compounds 4

The structures of the compounds **4** were characterized by NMR, IR, and MS spectroscopy. In the ^{13}C-NMR spectra of **4a**,**h**–**m**, the ylidic carbon appeared at δ 104.9–114.7, close to the corresponding chemical shift of compound **1** (δ 113.23) [2c]. In the IR spectra, two characteristic ester C=O stretching bands were observed at 1750–1667 cm^{-1}. The FABMS spectra showed a strong parent ion peak at $[M^+ + 1]$.

To obtain further information on structure, the crystal structures of **4a** and **4c** were determined by X-ray crystallography. The crystal data are summarized in Table 2, the selected bond lengths and angles are listed in Tables 3 and 4, and the ORTEP diagrams are illustrated in Figs. 1 and 2. The crystal structure of **4c** was found to consist of two isolated molecules, which are denoted here as **I** and **II**. The bismuth center in these ylides possesses a distorted tetrahedral geometry. The Bi–C_{ylide} bond lengths of **4a** and **4c** are in the range 2.178(7)–2.199(7) Å, slightly longer than that of **1** (2.156(11) Å) [6] and close to the Bi–C_{Ar} bond lengths (2.216(7)–2.225(8) Å for **4a** and 2.200(7)–2.231(7) Å for **4c**) as well as to the reported Bi–$C_{alkenyl}$ bond length (2.182(9) Å) in $[Ph_3BiCH{=}CMe_2]^+[BF_4]^-$ [11]. Therefore, the Bi–C_{ylide} bond in these ylides **4a**,**c** may reasonably be regarded as a polarized single bond, Bi^+–C^-, rather than a double bond, Bi=C.

As shown in Fig. 1, the carbon, nitrogen, and oxygen atoms of the alkylidene moiety in **4a** are on almost the same plane except for the ester group that includes the O(2), O(3), and C(6) atoms, which stand perpendicularly in relation to the plane, probably for electronic and steric reasons. The observed C(2)–C(3) bond length (1.45(1) Å) is close to that of a typical C–C single bond (1.48 Å), whereas the C(3)–C(4) bond length (1.35(1) Å) is close to that of a typical C=C double bond (1.32 Å) [12]. Furthermore, the C(4)–N bond length (1.358(9) Å) is close to that of a typical C–N single bond (1.38 Å) but much longer than that of a typical C=N double bond (1.28 Å). These findings are indicative of the considerable double bond character of the C(3)–C(4) bond as well as the considerable single bond character of the C(2)–C(3) and C(4)–N bonds.

The coordination environment around the bismuth center in **4a** is also noteworthy. The distance between the bismuth and nitrogen atoms (2.863(6) Å) is much longer than the sum of their covalent radii but shorter than the sum of their van der Waals radii (3.74 Å) [13]. In addition, the Bi–C(3)–C(4) bond angle of 109.5(5)° is smaller than the expected sp^2 bond angle. These data suggest the operation of some attractive interaction between the bismuth and nitrogen atoms.

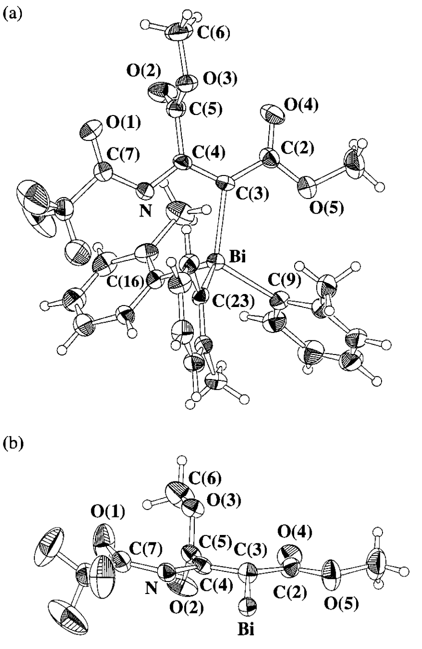


Fig. 1. (a) ORTEP diagram for **4a** (30% probability ellipsoids). (b) The alkylidene part of **4a**. The bismuth atom is included.

Table 4
Selected bond lengths (Å) and angles (°) of **4c**

Bond lengths		Bond angles	
*Molecule **I***			
Bi(1)–C(3)	2.190(7)	C(3)–Bi(1)–C(9)	115.0(3)
Bi(1)–C(9)	2.209(7)	C(3)–Bi(1)–C(16)	108.9(3)
Bi(1)–C(16)	2.231(7)	C(3)–Bi(1)–C(23)	115.1(3)
Bi(1)–C(23)	2.200(7)	C(9)–Bi(1)–C(16)	102.5(3)
C(2)–C(3)	1.46(1)	C(9)–Bi(1)–C(23)	102.6(3)
C(3)–C(4)	1.35(1)	C(16)–Bi(1)–C(23)	111.9(3)
C(4)–C(5)	1.531(10)	Bi(1)–C(3)–C(2)	124.5(5)
C(4)–N(1)	1.358(9)	Bi(1)–C(3)–C(4)	110.0(5)
C(7)–N(1)	1.363(9)	C(2)–C(3)–C(4)	125.5(7)
C(2)–O(4)	1.185(9)	C(3)–C(4)–C(5)	119.7(7)
C(2)–O(5)	1.356(9)	C(3)–C(2)–O(4)	126.7(7)
C(5)–O(2)	1.209(9)	C(3)–C(2)–O(5)	110.8(7)
C(5)–O(3)	1.326(9)	C(4)–C(5)–O(2)	123.7(7)
C(7)–O(1)	1.230(9)	C(3)–C(4)–N(1)	119.0(7)
Bi(1)···N(1)	2.896(6)	C(4)–N(1)–C(7)	119.8(6)
Bi(1)···O(5)	3.234(5)	N(1)–C(7)–O(1)	126.7(7)
*Molecule **II***			
Bi(2)–C(37)	2.178(7)	C(37)–Bi(2)–C(43)	123.2(3)
Bi(2)–C(43)	2.203(8)	C(37)–Bi(2)–C(50)	107.4(3)
Bi(2)–C(50)	2.213(8)	C(37)–Bi(2)–C(57)	108.1(3)
Bi(2)–C(57)	2.223(8)	C(43)–Bi(2)–C(50)	102.4(3)
C(36)–C(37)	1.446(10)	C(43)–Bi(2)–C(57)	103.4(3)
C(37)–C(38)	1.39(1)	C(50)–Bi(2)–C(57)	112.3(3)
C(38)–C(39)	1.531(10)	Bi(2)–C(37)–C(36)	109.7(5)
C(38)–N(3)	1.321(10)	Bi(2)–C(37)–C(38)	119.1(5)
C(41)–N(3)	1.382(10)	C(36)–C(37)–C(38)	130.9(7)
C(36)–O(11)	1.225(9)	C(37)–C(38)–C(39)	115.8(7)
C(36)–O(12)	1.321(9)	C(37)–C(36)–O(11)	121.9(7)
C(39)–O(9)	1.180(9)	C(37)–C(36)–O(12)	114.9(7)
C(39)–O(10)	1.331(10)	C(38)–C(39)–O(9)	123.7(8)
C(41)–O(8)	1.218(10)	C(37)–C(38)–N(3)	121.7(7)
Bi(2)···N(3)	3.239(6)	C(38)–N(3)–C(41)	117.4(7)
Bi(2)···O(11)	3.002(5)	N(3)–C(41)–O(8)	127.1(8)

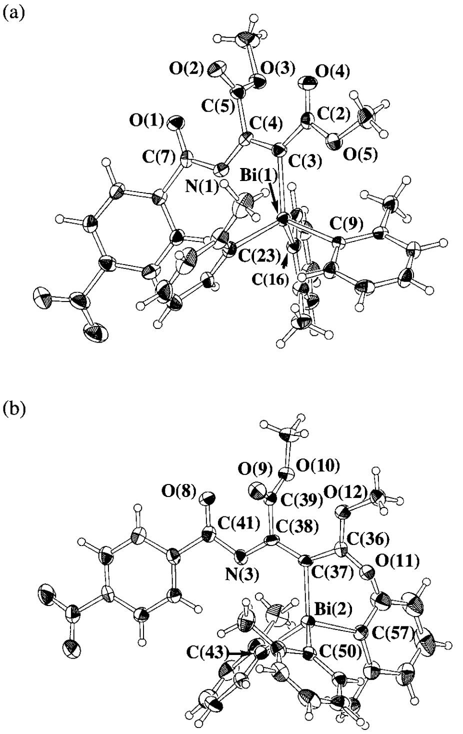


Fig. 2. ORTEP diagram for **4c** (30% probability ellipsoids). (a) Molecule **I**. (b) Molecule **II**.

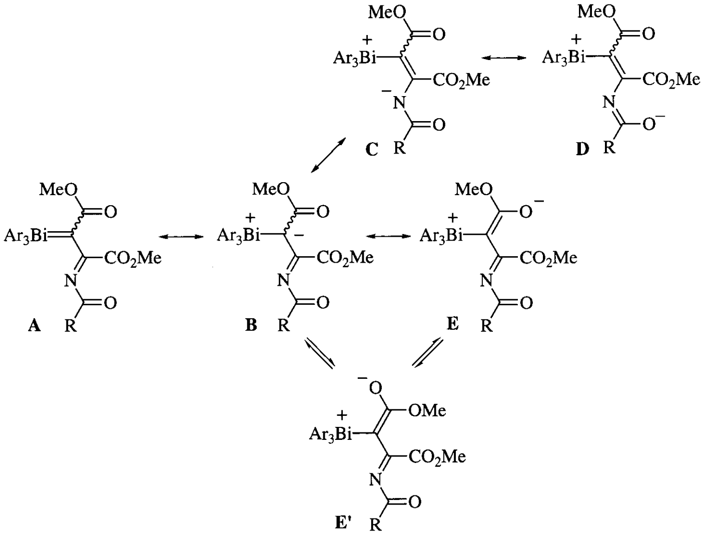
In Scheme 3, possible canonical structures of the bismuthonium ylides **4** are depicted, where the negative charge on the ylidic carbon is efficiently delocalized over the extended conjugative system present in the highly functionalized alkylidene moiety. The remarkable stability of the ylides **4** can be attributed to this efficient charge delocalization. The X-ray analysis data suggest considerable contribution from structures **C** and **D** to the actual bonding state in **4a**.

There is a structural dissimilarity between molecules **I** and **II** of **4c**. In molecule **I**, the ester carbonyl group C(2)=O(4) is directed opposite to the bismuth, and the Bi(1)···N(1) distance (2.896(6) Å) is much shorter than the Bi(1)···O(5) distance (3.234(5) Å), indicating that the bismuth interacts more strongly with imido nitrogen N(1) rather than the methoxy oxygen O(5). The coordination environment around the bismuth in **I** is similar to that of **4a**. In contrast, in molecule **II**, the ester carbonyl group C(36)=O(11) is directed toward the bismuth, and the Bi(2)···O(11) distance (3.002(5) Å) is somewhat shorter than the Bi(2)···N(3) distance (3.239(6) Å) [14], indicating that the bismuth interacts more strongly with the carbonyl oxygen atom O(11) rather than the imido nitrogen N(3).

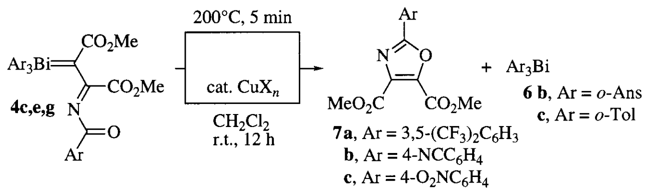
The differences in the coordination environment between **I** and **II** are also reflected in the bond lengths and angles of their respective alkylidene moieties. The Bi(1)–C(3)–C(4) bond angle (110.0(5)°) in **I** and the Bi(2)–C(37)–C(36) bond angle (109.7(5)°) in **II** are smaller than the value expected for sp^2 configuration, probably due to the attractive interaction between the bismuth and the nitrogen (N(1) for **I**) or oxygen (O(11) for **II**) atoms. The C(3)–C(4), C(7)–N(1), and C(2)–O(4) bond lengths in **I** are shorter than the corresponding bond lengths in **II**, C(37)–C(38), C(41)–N(3), and C(36)–O(11), whereas the C(2)–C(3), C(4)–N(1), and C(2)–O(5) bond lengths in **I** are longer than the corresponding bond lengths in **II**, C(36)–C(37), C(38)–N(3), and C(36)–O(12). These findings suggest the importance of the canonical structure **E**′ in the actual bonding state of **II** over the structure **E** against **I** (Scheme 3).

2.3. Reactions of compounds 4

When treated with two equivalents of acetic acid in CH_2Cl_2 at room temperature, the Bi–C_{ylide} bond of **4e** was cleaved to give olefin **5a** and tris(2-methoxyphenyl)bismuth diacetate (Eq. (2)). The stereochemistry of **5a** was assigned by ^{1}H-NMR spectroscopy as well as by X-ray crystallography. At the initial stages of this reaction, the (*E*)-isomer was formed predominantly. When stood in the reaction conditions or passed through a silica gel column, the (*E*)-isomer was gradually converted to the (*Z*)-isomer (Eq. (3)) [15]. Thus, the (*E*)-isomer is a kinetic product and the (*Z*)-isomer is a thermodynamic product. The thermodynamic stabilization of the (*Z*)-isomer may be attributed to the intramolecular hydrogen bonding between the NH proton and the ester oxygen [16]. The Bi–C_{ylide} bond of **4i** was cleaved by excess HClaq at room temperature, quantitatively affording tris(4-methylphenyl)-bismuth dichloride and the olefin **5b** (Eq. (4)). Ylide **4i** reacted with two equivalents of 4-nitrophenol within 2 h at room temperature to afford tris(4-methylphenyl)bismuth bis(4-nitrophenoxide) and the olefin **5b** in quantitative NMR yields (Eq. (5)). In contrast, 3,5-di-*tert*-butylphenol did not cleave the Bi–C_{ylide} bond of **4i** even after heating at 50°C for 50 h. 4-Nitrobenzenethiol was readily oxidized by 0.5 equivalents of **4i** to give bis(4-nitrophenyl) disulfide in 92%

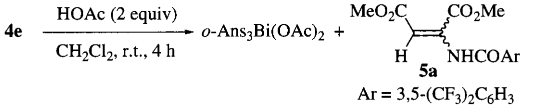


Scheme 3.

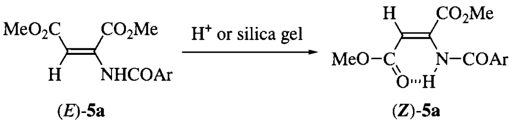


Scheme 4.

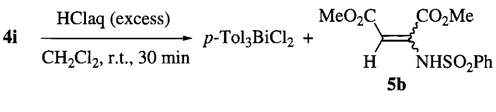
yield (Eq. (6)). In this reaction, tris(4-methylphenyl)bismuthane (**6a**) and olefin **5b** were obtained in good yields. In contrast to **1**, both **4e** and **4i** did not react with the aldehydes (PhCHO, 4-ClC$_6$H$_4$CHO, and 4-O$_2$NC$_6$H$_4$CHO) even after heating at 40–60°C for 1 week.



(2)



(3)



(4)

$$\mathbf{4i} \xrightarrow[\text{CDCl}_3,\ \text{r.t., 2 h}]{4\text{-O}_2\text{NC}_6\text{H}_4\text{OH (2 equiv)}} p\text{-Tol}_3\text{Bi(OC}_6\text{H}_4\text{-4-NO}_2)_2 + \mathbf{5b} \quad (5)$$

$$\mathbf{4i} \xrightarrow[\text{CDCl}_3,\ -78\ ^\circ\text{C to r.t.}]{4\text{-O}_2\text{NC}_6\text{H}_4\text{SH (2 equiv)}} (4\text{-O}_2\text{NC}_6\text{H}_4\text{S})_2 + \underset{\mathbf{6a}}{p\text{-Tol}_3\text{Bi}} + \mathbf{5b} \quad (6)$$

On thermolysis, or when decomposed in the presence of a copper catalyst, the bismuthonium ylides **4** bearing an *N*-aroyl group exhibited a novel mode of transformation (Scheme 4 and Table 5). Thus, when heated at 200°C for 5 min, ylide **4e** decomposed completely to yield tris(2-methoxyphenyl)bismuthane (**6b**) (quant), oxazole **7a** (96%), and olefin **5a** (4%). Under similar conditions, ylide **4g** gave bismuthane **6b** and oxazole **7b** in high yield. In the presence of a catalytic amount (10 mol%) of Cu(OTf)$_2$, ylide **4e** decomposed smoothly at room temperature to afford bismuthane **6b** and oxazole **7a**. Without the copper catalyst, ylide **4e** remained unchanged under the same conditions. Other copper salts such as Cu(OAc)$_2$, CuI, CuBr, and CuCl were also effective as catalysts for this transformation. Ylides **4g** and **4c** both bearing the *N*-aroyl group similarly decomposed in the presence of a catalytic amount of Cu(OTf)$_2$ to give oxazoles **7b** and **7c**, respectively, along with **6b** and **6c**.

Even in the presence of a trap or a hydrogen donor compound (10–20 equivalents) such as 3-hexyne, **3a**, cyclohexene, or 1,4-cyclohexadiene, both the thermolysis and the copper-catalyzed decomposition of **4e** afforded oxazole **7a** and bismuthane **6b** as the major products. Ogawa and Suzuki have reported the CuCl-catalyzed reaction of the stabilized ylide **1** with terminal acetylenes, which affords tetrahydrobenzofuran derivatives and dimedone in moderate yields [17]. In contrast, the CuCl-catalyzed decomposition of ylide **4e** in the presence of two equivalents of phenylacetylene gave oxazole **7a** in high yield. These results suggest that the intramolecular C–O bond formation occurs more rapidly than the intermolecular coupling with the carbon–carbon multiple bonds and the hydrogen abstraction from the additives or solvent. Presumably, the good nucleofugality of the triarylbismuthonio group in **4** would play an important role in the formation of the oxazoles. The copper salt may facilitate the cleavage of the Bi–C$_{\text{ylide}}$ bond via the oxidative addition or transmetallation, but the reaction pathway leading to the oxazoles is not clear at present. The thermolysis as well as the copper-catalyzed decomposition of the bismuthonium ylides **4** provides a new synthetic route to

Table 5
Synthesis of oxazoles **7** from bismuthonium ylides **4**

Entry	Ylide **4**	Method [a]	Catalyst (mol%)	Oxazole **7** (%) [b]	Ar$_3$Bi **6** (%) [b]	Olefin **5** (%) [b]
1	**4e**	T		**7a** (96)	**6b** (quant)	**5a** (4)
2	**4e**	C	Cu(OTf)$_2$ (10)	**7a** (67) [c]	**6b** (77) [c]	
3	**4e**	C	Cu(OAc)$_2$ (10)	**7a** (63)	**6b** (quant)	**5a** (trace)
4	**4e**	C	CuI (10)	**7a** (81)	**6b** (quant)	**5a** (4)
5	**4e**	C	CuBr (10)	**7a** (91)	**6b** (quant)	**5a** (5)
6	**4e**	C	CuCl (10)	**7a** (87)	**6b** (quant)	**5a** (3)
7	**4g**	T		**7b** (92)	**6b** (quant)	
8	**4g**	C	Cu(OTf)$_2$ (10)	**7b** (83) [c]	**6b** (86) [c]	
9	**4c**	C	Cu(OTf)$_2$ (12)	**7c** (91) [c]	**6c** (68) [c]	

[a] T, thermolysis (200°C, 5 min); C, copper-catalyzed decomposition (r.t., 12 h in CH$_2$Cl$_2$).

[b] NMR yields.

[c] Isolated yields.

2,4,5-trisubstituted oxazoles bearing two ester groups at the 4 and 5 positions [18].

3. Experimental

^{1}H- and ^{13}C-NMR (200 and 50.2 MHz, respectively) spectra were recorded on a Varian Gemini-200 spectrometer using $CDCl_3$ as the solvent unless otherwise noted. Chemical shifts are referenced to TMS (0 ppm) and coupling constants J are reported in Hz. IR spectra were observed as KBr pellets on a Shimadzu FTIR-8100S spectrophotometer. FABMS spectra were obtained on a JEOL JMS-HS110 spectrometer using 3-nitrobenzyl alcohol as a matrix. EIMS spectra were obtained on a Shimadzu QP2000 spectrometer. Melting points were measured on a Yanagimoto hot-stage apparatus and are uncorrected. Elemental analyses were performed at the Microanalytical Laboratory of Kyoto University. Dichloromethane (CH_2Cl_2) was distilled from CaH_2 under argon before use. Column chromatography was performed on silica gel (Wakogel C200). Iminotriaryl-λ^5-bismuthanes **2** were prepared by the KO-*t*-Bu-promoted reaction of triarylbismuth dichlorides and amides [8,19]. Compounds **2c**,**e**,**f**,**g**,**i**,**j** were used without isolation for subsequent reactions. All olefins and acetylenes employed were purified by distillation and stored over 4 Å molecular sieves. Copper halides (CuI, CuBr, CuCl) were purified according to the reported procedures [20]. Other reagents were used as commercially received. All reactions with air-sensitive compounds were carried out under an argon atmosphere.

*3.1. Synthesis of stabilized bismuthonium ylides (**4**): general procedure*

A mixture of iminotriaryl-λ^5-bismuthane (**2**) (3 mmol), dialkyl acetylenedicarboxylate (**3**) (6–15 mmol), 4 Å molecular sieves, and CH_2Cl_2 (30 ml) was stirred under the conditions summarized in Table 1. The mixture was filtered through Celite and the filtrate was concentrated under reduced pressure to leave an oily residue. The resulting residue was washed with hexane and chromatographed on a silica gel column (CH_2Cl_2) to elute crude bismuthonium ylide **4**, which was purified by recrystallization from CH_2Cl_2/hexane or EtOAc/pentane.

*3.1.1. Ylide **4a***

M.p. 168–171°C (dec.). ^{1}H-NMR: δ 2.31 (s, 9H), 3.48 (s, 3H), 3.96 (s, 3H), 7.31–7.46 (m, 9H), 7.67–7.71 (m, 3H). $^{13}C\{^1H\}$-NMR: δ 24.4, 51.8, 52.9, 114.7, 116.7 ($J_{C-F} = 288$), 128.8, 131.4, 132.1, 135.5, 142.7, 143.2, 164.0, 166.6. IR: ν_{max} 1742 (C=O), 1700 (C=O), 1646 (C=O), 1559, 1541, 1520, 1456, 1435, 1416, 1316, 1266, 1206, 1186, 1161, 1138, 1009, 978, 930, 903, 793, 777, 752, 718, 432, 419 cm^{-1}. FABMS: *m*/*z* 736 [$M^+ + 1$]. Anal. Calc. for $C_{29}H_{27}BiF_3NO_5$: C, 47.36; H, 3.70; N, 1.90. Found: C, 47.12; H, 3.74; N, 1.97%.

*3.1.2. Ylide **4b***

M.p. 174–178°C (dec.). ^{1}H-NMR: δ 2.34 (s, 9H), 3.48 (s, 3H), 4.02 (s, 3H), 7.14–7.24 (m, 3H), 7.34–7.47 (m, 6H), 7.68–7.76 (m, 4H), 8.01 (s, 2H). IR: ν_{max} 1746 (C=O), 1701 (C=O), 1630 (C=O), 1599, 1559, 1541, 1509, 1466, 1456, 1428, 1389, 1356, 1281, 1260, 1223, 1134, 1057, 1009, 986, 914, 905, 843, 818, 795, 774, 749, 696, 534, 432 cm^{-1}. FABMS: *m*/*z* 880 [$M^+ + 1$]. Anal. Calc. for $C_{36}H_{30}BiF_6NO_5$: C, 49.16; H, 3.44; N, 1.59. Found: C, 48.86; H, 3.44; N, 1.53%.

*3.1.3. Ylide **4c***

M.p. 170–172°C (dec.). ^{1}H-NMR: δ 2.36 (s, 9H), 3.49 (s, 3H), 4.01 (s, 3H), 7.23–7.30 (m, 3H), 7.38–7.45 (m, 6H), 7.52 (d, 2H, $J = 8.7$), 7.69 (d, 3H, $J = 7.8$), 7.77 (d, 2H, $J = 8.7$). IR: ν_{max} 1740 (C=O), 1688 (C=O), 1636 (C=O), 1617, 1590, 1522, 1499, 1480, 1433, 1372, 1348, 1320, 1275, 1238, 1206, 1100, 1048, 1013, 990, 938, 897, 878, 849, 787, 752, 733, 716, 644, 432 cm^{-1}. FABMS: *m*/*z* 789 [$M^+ + 1$]. Anal. Calc. for $C_{34}H_{31}BiN_2O_7$: C, 51.78; H, 3.96; N, 3.55. Found: C, 51.54; H, 4.09; N, 3.52%.

*3.1.4. Ylide **4d***

M.p. 207–210°C (dec.). ^{1}H-NMR: δ 3.37 (s, 3H), 3.60 (s, 9H), 3.96 (s, 3H), 7.04–7.16 (m, 6H), 7.42–7.50 (m, 3H), 7.68–7.72 (m, 3H). IR: ν_{max} 1746 (C=O), 1703 (C=O), 1640 (C=O), 1582, 1570, 1524, 1472, 1433, 1404, 1304, 1271, 1242, 1208, 1179, 1129, 1048, 1017, 1005, 976, 939, 901, 847, 789, 777, 758, 669, 478, 432 cm^{-1}. FABMS: *m*/*z* 784 [$M^+ + 1$]. Anal. Calc. for $C_{29}H_{27}BiF_3NO_8$: C, 44.46; H, 3.47; N, 1.79. Found: C, 44.19; H, 3.42; N, 1.82%.

*3.1.5. Ylide **4e***

M.p. 175–177°C (dec.). ^{1}H-NMR: δ 3.36 (s, 3H), 3.64 (s, 9H), 4.03 (s, 3H), 6.94–7.07 (m, 6H), 7.35–7.43 (m, 3H), 7.63 (s, 1H), 7.76 (d, 3H, $J = 8.3$), 8.01 (s, 2H). IR: ν_{max} 1732 (C=O), 1692 (C=O), 1628 (C=O), 1595, 1568, 1514, 1471, 1433, 1389, 1356, 1279, 1225, 1177, 1130, 1063, 1048, 987, 907, 843, 820, 789, 776, 754, 698, 681, 478, 434 cm^{-1}. FABMS: *m*/*z* 928 [$M^+ + 1$]. Anal. Calc. for $C_{36}H_{30}BiF_6NO_8$: C, 46.61; H, 3.26; N, 1.51. Found: C, 46.50; H, 3.13; N, 1.50%.

*3.1.6. Ylide **4f***

M.p. 158–162°C (dec.). ^{1}H-NMR: δ 3.36 (s, 3H), 3.64 (s, 9H), 4.02 (s, 3H), 6.99–7.10 (m, 6H), 7.38–7.47 (m, 3H), 7.55 (d, 2H, $J = 9.1$), 7.70–7.77 (m, 5H). IR: ν_{max} 1750 (C=O), 1717 (C=O), 1686 (C=O), 1617, 1590, 1559, 1541, 1522, 1509, 1472, 1458, 1433, 1362, 1341, 1298, 1273, 1240, 1161, 1113, 1048, 1017, 899, 851, 785, 752, 729, 669, 419 cm^{-1}. FABMS: m/z 837 [M$^+$ + 1]. Anal. Calc. for $C_{34}H_{31}BiN_2O_{10}$: C, 48.81; H, 3.73; N, 3.35. Found: C, 48.55; H, 3.71; N, 3.63%.

3.1.7. Ylide ***4g***

M.p. 179–181°C (dec.). ^{1}H-NMR: δ 3.36 (s, 3H), 3.63 (s, 9H), 4.01 (s, 3H), 6.99–7.09 (m, 6H), 7.14–7.28 (m, 3H), 7.39–7.51 (m, 4H), 7.71 (m, 3H, $J = 7.3$). IR: ν_{max} 1750 (C=O), 1736 (C=O), 1676 (C=O), 1609, 1568, 1559, 1512, 1493, 1472, 1433, 1358, 1300, 1275, 1240, 1210, 1177, 1163, 1102, 1048, 1017, 939, 897, 860, 787, 774, 750, 569, 550, 477, 428 cm^{-1}. FABMS: m/z 817 [M$^+$ + 1]. Although spectroscopic data clearly supported a high state of purity of **4g**, we were not successful in obtaining satisfactory analytical data.

3.1.8. Ylide ***4h***

M.p. 196–198°C (dec.). ^{1}H-NMR: δ 2.42 (s, 9H), 3.47 (s, 3H), 3.93 (s, 3H), 7.38 (d, 6H, $J = 7.9$), 7.59 (d, 6H, $J = 7.9$). ^{13}C{^{1}H}-NMR: δ 21.5, 52.0, 53.3, 110.0, 119.7 ($J_{CF} = 323$), 132.2, 135.4, 135.6, 142.1, 163.9, 165.7, 166.3. IR: ν_{max} 1742 (C=O), 1684 (C=O), 1509, 1490, 1433, 1374, 1335, 1264, 1227, 1220–1150, 1127, 1065, 1007, 982, 959, 885, 835, 799, 735, 700, 646, 617, 583, 558, 507, 475 cm^{-1}. FABMS: m/z 772 [M$^+$ + 1]. Anal. Calc. for $C_{28}H_{27}BiF_3NO_6S$: C, 43.59; H, 3.53; N, 1.82. Found: C, 42.95; H, 3.53; N, 1.82%.

3.1.9. Ylide ***4i***

M.p. 155–156°C (dec.). ^{1}H-NMR: δ 2.39 (s, 9H), 3.42 (s, 3H), 4.00 (s, 3H), 7.08–7.20 (m, 2H), 7.26 (d, 6H, $J = 8.0$), 7.30 (m, 1H), 7.50 (m, 2H), 7.53 (d, 6H, $J = 8.0$). ^{13}C{^{1}H}-NMR: δ 21.5, 51.4, 53.2, 104.9, 126.5, 128.0, 130.5, 131.9, 135.4, 136.3, 141.5, 143.4, 163.3, 167.2, 167.5. IR: ν_{max} 1742 (C=O), 1669 (C=O), 1474, 1435, 1405, 1392, 1300, 1260, 1208, 1185, 1144, 1086, 1067, 1007, 980, 955, 874, 822, 801, 752, 735, 714, 689, 633, 608, 560, 538, 477 cm^{-1}. FABMS: m/z 780 [M$^+$ + 1]. Anal. Calc. for $C_{33}H_{32}BiNO_6S \cdot CH_2Cl_2$: C, 47.23; H, 3.96; N, 1.62. Found: C, 47.67; H, 3.81; N, 1.60%.

3.1.10. Ylide ***4j***

M.p. 188–190°C (dec.). ^{1}H-NMR: δ 2.32 (s, 3H), 3.40 (s, 3H), 4.01 (s, 3H), 6.94 (d, 2H, $J = 8.2$), 7.37 (d, 2H, $J = 8.2$), 7.44–7.54 (m, 9H), 7.63–7.73 (m, 6H). ^{13}C{^{1}H}-NMR: δ 21.4, 51.3, 53.2, 105.1, 126.4, 128.7, 131.1, 131.3, 135.7, 139.9, 140.3, 141.0, 163.2, 167.0, 167.5. IR: ν_{max} 1742 (C=O), 1674 (C=O), 1568, 1507, 1474, 1433, 1393, 1374, 1268, 1211, 1180, 1144, 1086, 1065, 994, 955, 880, 826, 810, 800, 740, 687, 668, 631, 586, 552, 538, 444 cm^{-1}. FABMS: m/z 752 [M$^+$ + 1]. Anal. Calc. for $C_{31}H_{28}BiNO_6S$: C, 49.54; H, 3.75; N, 1.86. Found: C, 49.29; H, 3.75; N, 1.86%.

3.1.11. Ylide ***4k***

M.p. 158–159°C. ^{1}H-NMR: δ 0.91 (t, 3H, $J = 7.1$), 1.39 (t, 3H, $J = 7.2$), 2.42 (s, 9H), 4.00 (q, 2H, $J = 7.1$), 4.40 (q, 2H, $J = 7.2$), 7.38 (d, 6H, $J = 8.0$), 7.60 (d, 6H, $J = 8.0$). ^{13}C{^{1}H}-NMR: δ 13.7, 13.8, 21.5, 61.4, 62.7, 110.3, 119.7 ($J_{CF} = 323$), 132.2, 135.4, 135.8, 142.1, 163.8, 165.2, 166.0. IR: ν_{max} 1728 (C=O), 1694 (C=O), 1538, 1489, 1448, 1393, 1374, 1337, 1262, 1227, 1220–1150, 1130, 1057, 1020, 1005, 928, 893, 849, 799, 762, 741, 644, 610, 585, 507, 475 cm^{-1}. FABMS: m/z 800 [M$^+$ + 1]. Anal. Calc. for $C_{30}H_{31}BiF_3NO_6S$: C, 45.06; H, 3.91; N, 1.75. Found: C, 44.96; H, 3.87; N, 1.82%.

3.1.12. Ylide ***4l***

M.p. 88–90°C. ^{1}H-NMR: δ 0.86 (t, 3H, $J = 7.1$), 1.44 (t, 3H, $J = 7.1$), 2.38 (s, 9H), 3.95 (q, 2H, $J = 7.1$), 4.47 (q, 2H, $J = 7.1$), 7.08–7.18 (m, 2H), 7.20–7.35 (m, 7H), 7.47–7.54 (m, 2H), 7.55 (d, 6H, $J = 8.2$). ^{13}C{^{1}H}-NMR: δ 13.8, 13.9, 21.5, 60.5, 62.5, 104.1, 126.4, 127.9, 130.4, 131.3, 135.5, 136.6, 141.4, 143.6, 163.3, 167.0, 167.9. IR: ν_{max} 1740 (C=O), 1673 (C=O), 1474, 1445, 1406, 1358, 1302, 1258, 1202, 1186, 1146, 1086, 1059, 1007, 912, 885, 841, 793, 752, 731, 712, 689, 629, 600, 569, 540, 477 cm^{-1}. FABMS: m/z 808 [M$^+$ + 1]. Anal. Calc. for $C_{35}H_{36}BiNO_6S$: C, 52.05; H, 4.49; N, 1.73. Found: C, 51.61; H, 4.51; N, 1.84%.

3.1.13. Ylide ***4m***

M.p. 196–198°C (dec.). ^{1}H-NMR: δ 0.82 (t, 3H, $J = 7.1$), 1.44 (t, 3H, $J = 7.1$), 2.31 (s, 3H), 3.93 (q, 2H, $J = 7.1$), 4.47 (q, 2H, $J = 7.1$), 6.92 (d, 2H, $J = 8.1$), 7.37 (d, 2H, $J = 8.1$), 7.43–7.52 (m, 9H), 7.64–7.75 (m, 6H). ^{13}C{^{1}H}-NMR: δ 13.8, 13.9, 21.4, 60.5, 62.5, 106.0, 126.4, 128.7, 131.0, 131.3, 135.7, 140.2, 140.5, 140.9, 163.2, 166.7, 167.0. IR: ν_{max} 1736 (C=O), 1667 (C=O), 1568, 1485, 1435, 1397, 1356, 1298, 1285, 1256, 1211, 1144, 1080, 1059, 1018, 994, 914, 882, 841, 818, 787, 741, 727, 685, 662, 617, 590, 552, 542, 448, 438 cm^{-1}. FABMS: m/z 780 [M$^+$ + 1]. Anal. Calc. for $C_{33}H_{32}BiNO_6S$: C, 50.84; H, 4.14; N, 1.80. Found: C, 50.52; H, 4.17; N, 1.83%.

3.2. Reaction of ***4e*** *with AcOH*

Acetic acid (6.4 μl, 0.11 mmol) was added to a CH_2Cl_2 solution (5 ml) of **4e** (46 mg, 0.050 mmol), and the resulting mixture was stirred for 4 h at room temperature (r.t.). The solution was evaporated to leave an oily residue, which was chromatographed on silica gel to afford tris(2-methoxyphenyl)bismuth diacetate (32 mg, 100%) and two separate isomers of olefin **5a** (total 20 mg, 100%; $E/Z = 40/60$ before column chromatography; 20/80 after column chromatography). The stereochemistry of **5a** was assigned on the basis of the solvent effect on the chemical shift of the NH proton in ^{1}H-NMR. According to the change in solvent polarity, the N*H* peak of the (*E*)-isomer should vary considerably, whereas the corresponding peak of the (*Z*)-isomer should be indifferent because the NH proton is intramolecularly hydrogen-bonded to the ester oxygen. The olefin obtained from the earlier eluates showed the NH proton at δ 11.31 in $CDCl_3$ and δ 11.00 in DMSO-d_6, whereas the olefin from the later eluates showed the NH proton at δ 8.61 in $CDCl_3$ and δ 11.27 in DMSO-d_6. Therefore, the former olefin was assigned to the (*Z*)-isomer and the latter to the (*E*)-isomer. The (*Z*)-geometry of the former olefin was further confirmed by X-ray analysis, although the collected data was insufficient in quality for discussing the bond parameters. The (*E*)-isomer was formed predominantly at the initial stages of this reaction, and it was found to isomerize to the (*Z*)-isomer under the reaction conditions.

3.2.1. Dimethyl 2-{N-[3,5-bis(trifluoromethyl)benzoyl]}-aminofumarate (**5a**; (Z)-isomer)

M.p. 106–108°C. ^{1}H-NMR: δ 3.83 (s, 3H), 3.92 (s, 3H), 5.78 (s, 1H), 8.11 (s, 1H), 8.38 (s, 2H), 11.31 (s, 1H). ^{1}H-NMR (DMSO-d_6): δ 3.71 (s, 3H), 3.76 (s, 3H), 6.20 (s, 1H), 8.46 (s, 1H), 8.58 (s, 2H), 11.00 (s, 1H). IR: ν_{max} 1736, 1701, 1690, 1638, 1458, 1433, 1277, 1229, 1194, 1129, 1115, 1019, 962, 924, 907, 853, 799, 756, 700, 683. EIMS: *m/z* 340 [$M^+ - CO_2Me$], 241, 213. Anal. Calc. for $C_{15}H_{11}F_6NO_5$: C, 45.13; H, 2.78; N, 3.51. Found C, 45.31; H, 2.62; N, 3.24%.

3.2.2. Dimethyl 2-{N-[3,5-bis(trifluoromethyl)benzoyl]}-aminomaleate (**5a**; (E)-isomer)

^{1}H-NMR: δ 3.79 (s, 3H), 3.95 (s, 3H), 7.13 (s, 1H), 8.07 (s, 1H), 8.28 (s, 2H), 8.61 (s, 1H). ^{1}H-NMR (DMSO-d_6): δ 3.64 (s, 3H), 3.78 (s, 3H), 6.13 (s, 1H), 8.43 (s, 1H), 8.54 (s, 2H), 11.27 (s, 1H). IR: ν_{max} 1724, 1701, 1653, 1636, 1458, 1444, 1437, 1323, 1280, 1259, 1174, 1130, 970, 912, 874, 862, 820, 762, 700, 683.

3.2.3. Tris(2-methoxyphenyl)bismuth diacetate

M.p. 145–146°C (lit. [21] 147°C). ^{1}H-NMR: δ 1.68 (s, 6H), 3.87 (s, 9H), 7.15–7.23 (m, 6H), 7.39–7.47 (m, 3H), 8.20 (d, 3H, $J = 7.0$).

3.3. Reaction of **4i** with aqueous HCl

Aqueous HCl (ca. 3 M, 0.50 ml) was added to a CH_2Cl_2 solution (5 ml) of **4i** (133 mg, 0.171 mmol), and the resulting mixture was stirred vigorously for 30 min at r.t. The organic phase was separated, dried over $MgSO_4$, and evaporated to leave a mixture of tris(4-methylphenyl)bismuth dichloride (100%) and olefin **5b** (100%; $E/Z =$ ca. 1/5). The stereochemistry of **5b** was characterized on the basis of the solvent effect on the chemical shift of its NH proton (see above). The (*Z*)-isomer of **5b** could be isolated by column chromatography on silica gel, whereas the (*E*)-isomer could not.

3.3.1. Dimethyl 2-[N-(phenylsulfonyl)]aminofumarate (**5b**; (Z)-isomer)

M.p. 99–100°C. ^{1}H-NMR: δ 3.76 (s, 3H), 3.80 (s, 3H), 5.77 (s, 1H), 7.49–7.69 (m, 3H), 7.90–8.00 (m, 2H), 10.30 (s, 1H). ^{1}H-NMR (DMSO-d_6): δ 3.64 (s, 3H), 3.65 (s, 3H), 5.47 (s, 1H), 7.58–7.85 (m, 5H), 10.25 (s, 1H). IR: ν_{max} 1740, 1696, 1640, 1437, 1406, 1335, 1285, 1219, 1130, 1086, 1022, 955, 899, 876, 847, 779, 737, 689, 660, 600, 554, 505, 453 cm^{-1}. EIMS: *m/z* 299 [M^+]. Anal. Calc. for $C_{12}H_{13}NO_6S$: C, 48.16; H, 4.38; N, 4.68. Found: C, 48.32; H, 4.41; N, 4.68%.

3.3.2. Dimethyl 2-[N-(phenylsulfonyl)]aminomaleate (**5b**; (E)-isomer)

^{1}H-NMR: δ 3.84 (s, 3H), 3.89 (s, 3H), 6.11 (s, 1H), 7.45–7.70 (m, 3H), 7.88–7.95 (m, 2H). The NH proton was not assigned.

3.4. Reaction of **4i** with 4-nitrophenol

A mixture of 4-nitrophenol (3.7 mg, 0.27 mmol), **4i** (9.5 mg, 0.012 mmol), and $CDCl_3$ (0.50 ml) was allowed to stand in an NMR tube at r.t. After 2 h, tris(4-methylphenyl)bismuth bis(4-nitrophenoxide) and olefin **5b** ($E/Z = 3/97$) were formed in quantitative NMR yields. The (*E*)-isomer of **5b** was found to isomerize to the (*Z*)-isomer under the reaction conditions. Tris(4-methylphenyl)bismuth bis(4-nitrophenoxide) was identified by comparison with the authentic sample, prepared from tris(4-methylphenyl)bismuth dichloride and 4-nitrophenol in the presence of two equivalents of KO-*t*-Bu: M.p. 175–178°C (dec.). ^{1}H-NMR: δ 2.43 (s, 9H), 6.27 (d, 4H, $J = 9.0$), 7.43 (d, 6H, $J = 8.2$), 7.83 (d, 4H, $J = 9.0$), 7.91 (d, 6H, $J = 8.2$). $^{13}C\{^1H\}$-NMR: δ 21.5, 120.1, 126.0, 132.6, 134.3, 138.2, 143.0, 148.7, 170.0. IR: ν_{max} 1578 (NO_2), 1483, 1331, 1285, 1266 (NO_2), 1169, 1109, 1000, 862, 849, 820, 795, 756, 700, 646, 475 cm^{-1}. FABMS: *m/z* 634 [$Tol_3BiOCH_2C_6H_4NO_2^+$], 391, 300, 209. Anal. Calc. for $C_{33}H_{29}BiN_2O_6$: C, 52.25; H, 3.85; N, 3.69. Found C, 52.18; H, 3.91; N, 3.59%.

3.5. Reaction of **4i** with 4-nitrobenzenethiol

To a CH_2Cl_2 solution (5 ml) of 4-nitrobenzenethiol (29 mg, 0.19 mmol) was added **4i** (70 mg, 0.090 mmol) at −78°C, and the mixture was allowed to warm to r.t. with vigorous stirring. The resulting colorless solution was concentrated under reduced pressure to leave a crystalline solid, which was recrystallized from CH_2Cl_2/hexane to give bis(4-nitrophenyl) disulfide in 92% yield (27 mg). Bismuthane **6a** and olefin **5b** were obtained in 94 and 92% yields, respectively.

3.5.1. Bis(4-nitrophenyl) disulfide

M.p. 184–187°C (dec.) (lit. [22] 184–186°C). ^{1}H-NMR: δ 7.62 (d, 4H, $J = 8.8$), 8.20 (d, 4H, $J = 8.8$). EIMS: m/z 308 [M$^+$].

3.6. Thermolysis of **4e** and **4g**

An ampoule containing **4** was sealed off under vacuum and heated at 200°C in an oil bath for 5 min. After cooling, the product was dissolved in $CDCl_3$ and examined by ^{1}H-NMR. Oxazole **7** was formed in high yield (96% for **7a** and 92% for **7b**) with a quantitative recovery of tris(2-methoxyphenyl)bismuthane **6b**. Even in the presence of ten equivalents of 1,4-cyclohexadiene, thermal decomposition of **4e** (200°C, 5 min) led to the quantitative formation of **6b** and **7a**.

3.6.1. Dimethyl 2-[3,5-bis(trifluoromethyl)phenyl]-oxazole-4,5-dicarboxylate (**7a**)

^{1}H-NMR: δ 4.04 (s, 6H), 8.06 (s, 1H), 8.63 (s, 2H). IR: ν_{max} 1744, 1626, 1584, 1561, 1443, 1429, 1391, 1354, 1279, 1229, 1186, 1144, 1111, 1100, 1073, 961, 907, 847, 835, 797, 768, 739, 714, 700, 683, 432, 409 cm^{-1}. EIMS: 397 [M$^+$]. Anal. Calc. for $C_{15}H_9F_6NO_5$: C, 45.35; H, 2.28; N, 3.53. Found: C, 45.19; H, 2.11; N, 3.03%. This compound decomposed on heating and did not show a definite melting point.

3.6.2. Dimethyl 2-(4-cyanophenyl)oxazole-4,5-dicarboxylate (**7b**)

M.p. 174–175°C (lit. [18c] 174–175°C). ^{1}H-NMR: δ 4.02 (s, 6H), 7.81 (d, 2H, $J = 8.4$), 8.30 (d, 2H, $J = 8.4$). IR: ν_{max} 2234, 1757, 1734, 1578, 1545, 1491, 1445, 1412, 1354, 1320, 1231, 1196, 1146, 1088, 1067, 961, 851, 833, 799, 741, 704, 669, 552 cm^{-1}. EIMS: 286 [M$^+$].

3.7. Copper-catalyzed decomposition of **4c**, **4e**, and **4g**

A mixture of **4e** (105 mg, 0.113 mmol), $Cu(OTf)_2$ (4.1 mg, 0.011 mmol), and CH_2Cl_2 (3 ml) was stirred at r.t. for 12 h, and then concentrated under reduced pressure. The oily residue was chromatographed on a silica gel column (hexane/EtOAc = 10/1) to give bismuthane **6b** (40.3 mg, 67%) and oxazole **7a** (34.5 mg, 77%). Other copper salts such as $Cu(OAc)_2$, CuI, CuBr, and CuCl were also found to be effective as catalysts. The $Cu(OTf)_2$-catalyzed reaction of **4g** and **4c** afforded oxazoles **7b** and **7c**, respectively, in the yields listed in Table 5. Even in the presence of 3-hexyne (ten equivalents), **3a** (ten equivalents), cyclohexene (20 equivalents), 1,4-cyclohexadiene (ten equivalents), or phenylacetylene (two equivalents), the copper-catalyzed decomposition of **4e** (in CH_2Cl_2 at r.t. for 12 h with 10 mol% of $Cu(OTf)_2$ or CuCl) gave only bismuthane **6b** and the oxazole **7a** as the major products, although the decrease in conversion of **4e** was observed in some cases.

3.7.1. Dimethyl 2-(4-nitrophenyl)oxazole-4,5-dicarboxylate (**7c**)

M.p. 165–168°C. ^{1}H-NMR: δ 4.03 (s, 6H), 8.37 (s, 4H). IR: ν_{max} 1746, 1732, 1582, 1557, 1518, 1439, 1414, 1363, 1347, 1312, 1294, 1269, 1227, 1183, 1144, 1111, 1088, 1067, 961, 874, 855, 830, 797, 770, 719 cm^{-1}. EIMS: 306 [M$^+$]. Anal. Calc. for $C_{13}H_{10}N_2O_7$: C, 50.99; H, 3.29; N, 9.15. Found: C, 50.90; H, 3.47; N, 9.20%.

3.8. X-ray crystal structure analyses of **4a** and **4c**

Single crystals, grown from a 1:1 mixture of EtOAc/pentane at 4°C, were used for the X-ray crystallographic analyses. Intensity data were collected on a Rigaku AFC7S diffractometer at 23°C with graphite-monochromated Mo–K$_\alpha$ ($\lambda = 0.71069$ Å) radiation, using an ω–2θ scan technique to a maximum 2θ value of 55.0°.

For **4a**: scans of $(1.63 + 0.30 \tan \theta)°$ were made at a speed of 8.0° min^{-1}. The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by 14.1%. A linear correction factor was applied to data to account for this phenomenon. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.90 to 1.00.

For **4c**: scans of $(0.94 + 0.30 \tan \theta)°$ were made at a speed of 4.0° min^{-1}. The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by 17.7%. A linear correction factor was applied to data to account for this phenomenon. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.63 to 1.00. The data of all compounds were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied.

The structures were solved by direct methods (SIR-92) [23] and expanded using Fourier techniques (DIRDIF-94) [24]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral atom scattering factors were taken from Cromer and Waber [25]. Anomalous dispersion effects were included in F_{calc} [26]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [27]. The values for the mass attenuation coefficients are those of Creagh and Hubbell [28]. All calculations were performed using the TEXSAN [29] crystallographic software package of Molecular Structure Corporation. Further details of the crystal structure are provided in Tables 1 and 2 and have been deposited at the Cambridge Crystallographic Data Centre.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC-141067 for **4a** and CCDC-141118 for **4c**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Priority Area (A), 'The Chemistry of Inter-element Linkage' (no. 11120224), from the Ministry of Education, Science, Sports and Culture of Japan.

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