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Articles

A Stabilized Triarylbismuthane Imide: Synthesis and First X-ray Structure Analysis

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The synthesis and reactions of the first moisture-insensitive triarylbismuthane imide (**7**), bearing an oxazoline ring at a position *ortho* to the carbon bearing the bismuth atom, are described. The first X-ray crystallographic study of bismuthane imide has been carried out for compound **7**, which revealed that the bismuth center possesses a distorted-trigonal-bipyramidal geometry and the Bi−N(imide) bond length (2.13(1) Å) falls in the range of known Bi−N single bonds, suggesting a polarized $Bi^+{-}N^-$ bond rather than a $Bi{=}N$ double bond.

Introduction

Bismuthane imides of the general formula $R_3Bi{=}NE$ are the bismuth analogues of phosphane imides $R_3P{=}NE$, which have long been known as intermediates in the Staudinger and aza-Wittig reactions.[1] In contrast to the analogous compounds derived from lighter group 15 and 16 elements, bismuthane imides have remained almost unexamined until recently. The first synthesis of bismuthane imide was reported in 1964 by Wittig and Hellwinkel, who obtained triphenylbismuthane [(4-methylphenyl)sulfonyl]imide (**1**; $Ph_3Bi{=}NTs$; Ts = 4-$MeC_6H_4SO_2$) as a moisture-sensitive solid by treating triphenylbismuthane (Ph_3Bi) with anhydrous Chloramine-T in boiling acetonitrile.[2] The reactivity of this and related triarylbismuthane imides toward electrophiles has been examined for aldehydes, benzoyl chloride, and phenyl isocyanate.[3] The reaction of triarylbismuthanes with the iminoiodobenzene $PhI{=}NTs$[4] is convenient for the *in situ* generation of bismuthane imides,[5] while the metathesis between triarylbismuth dihalides and sulfonamides is also efficient for the preparation of similar imides.[6] All known bismuthane imides have a sulfonyl group on the imido nitrogen atom and are thereby thermally stabilized. These imides gradually decompose in air due to their moisture instability, although they can be stored over a period of weeks under dry nitrogen.[3,6] Since they also decompose slowly in solution, it is not easy to obtain pure bismuthane imides by recrystallization.

We report herein the synthesis and first X-ray structure analysis of a highly stabilized bismuthane imide, [2-(4,4-dimethyl-2-oxazolin-2-yl)phenyl]bis(4-methylphenyl)bismuthane [(trifluoromethyl)sulfonyl]imide (**7**), bearing an oxazoline ring as the intramolecularly coordinating group at the position *ortho* to the carbon bonded to bismuth.

Results and Discussion

Imide **7** was obtained in four steps, starting from tris(4-methylphenyl)bismuthane (Tol_3Bi); treatment of bis(4-methylphenyl)bismuth trifluoromethanesulfonate−hexamethylphosphoric triamide (HMPA) complex ($Tol_2BiOTf{\cdot}2HMPA$; Tf = CF_3SO_2) with an excess of [2-(4,4-dimethyl-2-oxazolin-2-yl)phenyl]magnesium bromide (**2**) gave the corresponding mixed triarylbismuthane **3** in 63% yield.[7] Bismuthane **3** was less stable than Tol_3Bi and readily decomposed during column chromatography on alumina or silica gel using chloroform as the eluent. Nevertheless, chloro[2-(4,4-dimethyl-2-oxazolin-2-yl)phenyl](4-methylphenyl)bismuthane (**4**) was obtained in good yield. As with other halobismuthanes containing an intramolecularly coordinating group,[8] compound **4** was moisture-insensitive. Bismuthane **3** was converted by the action of phenyliodine dichloride ($PhICl_2$) to the

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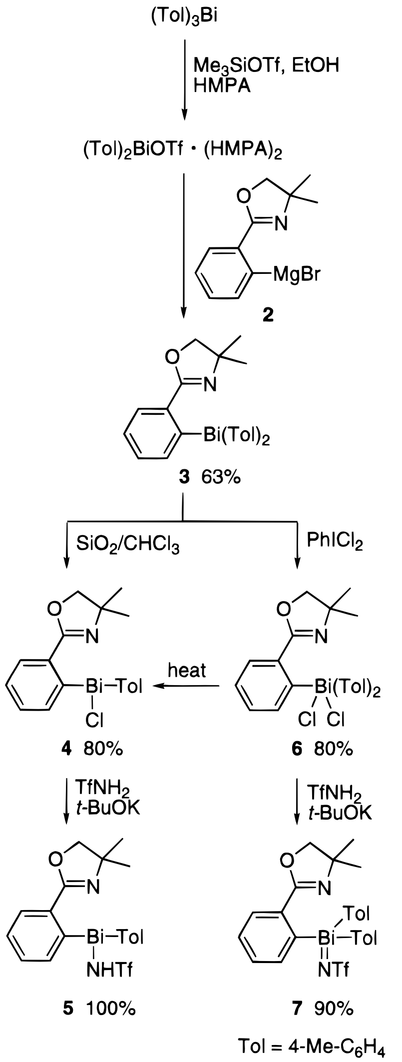
Scheme 1



Tol = 4-Me-C_6H_4
Tf = CF_3SO_2

corresponding dichloride **6** in 80% yield. When it was gently heated in an organic solvent, dichloride **6** slowly decomposed to give chlorobismuthane **4**. On treatment with a 2:1 molar ratio of potassium *tert*-butoxide (*t*-BuOK) and trifluoromethanesulfonamide ($TfNH_2$) in tetrahydrofuran (THF) at room temperature, dichloride **6** gave the corresponding bismuthane imide **7** in 90% yield, while chlorobismuthane **4** was converted to the amidobismuthane **5** by the action of a 1:1 molar mixture of *t*-BuOK and $TfNH_2$ (Scheme 1). In contrast to bis(4-methylphenyl)[*N*-(4-methylphenyl)sulfonamido]bismuthane ($Tol_2BiNHTs$),[5] compound **5** was thermally stable and did not disproportionate when left to stand in solution. All new organobisumuth compounds **3**–**7** were fully characterized by ^1H and ^{13}C NMR and IR spectroscopy as well as by elemental analyses.

The imide **7** is soluble in dichloromethane, chloroform, and THF but poorly soluble in diethyl ether and hexane; it can be readily purified by recrystallization from a dichloromethane–diethyl ether mixture. Compound **7** is not sensitive to moisture and can be handled under atmospheric conditions. After several months of storage on a bench shelf, crystals of imide **7** were still intact. In marked contrast to the known bismuthane imides,[3] it did not show any sign of decomposition when allowed to stand in $CDCl_3$. When heated around 200 °C under reduced pressure (1 mmHg) for 10 min, imide **7** decomposed to give amidobismuthane **5** as the major product (Scheme 2). Below 180 °C, no significant change was observed.

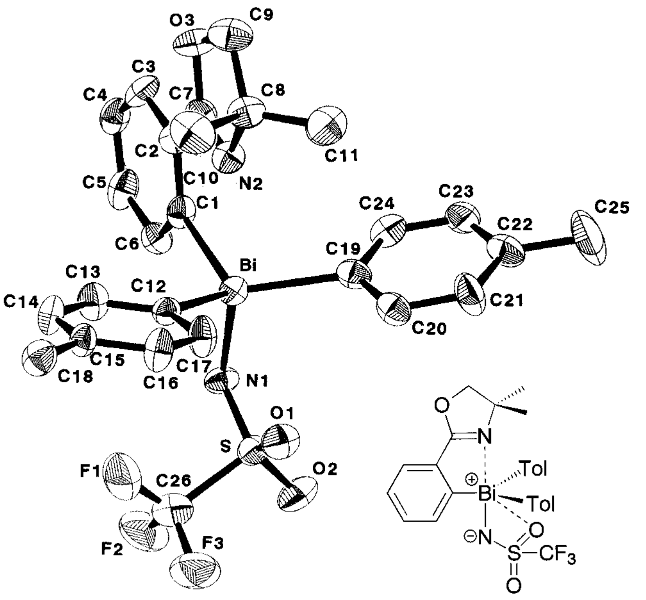
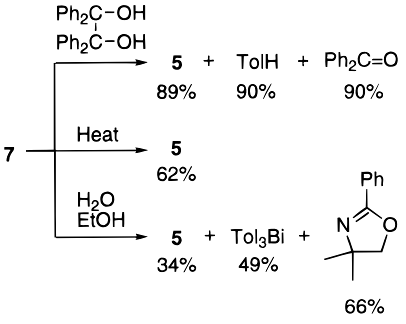


Figure 1. ORTEP drawing of compound **7**, with the crystallographic numbering scheme. The percentage probability level of the ellipsoids in this drawing is 30%.

Scheme 2



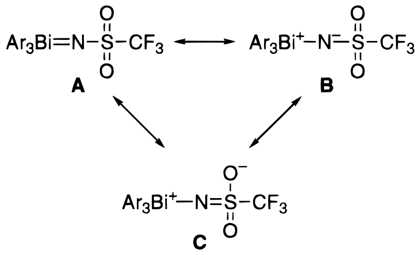
Although imide **1** is easily hydrolyzed to give triphenylbismuthane oxide ($Ph_3Bi{=}O$),[6] imide **7** underwent slow hydrolysis in boiling ethanol, giving a mixture of Tol_3Bi, amidobismuthane **5**, and 2-(4,4-dimethyl-2-oxazolin-2-yl)benzene in 49, 34, and 66% yields, respectively, based on imide **7**. While a bismuthane imide ($Tol_3Bi{=}NTs$) oxidized benzopinacol to benzophenone in almost quantitative yield within 30 min at room temperature,[5] it required 24 h for imide **7** to complete the oxidation. In the former case, Tol_3Bi and $TsNH_2$ were recovered in good yields, while in the latter case benzophenone, amidobismuthane **5**, and toluene were all obtained in around 90% yields with no bismuthane **3** being formed. These results clearly show that the introduction of an oxazoline ring at the position *ortho* to the carbon bonded to bismuth changes not only the reactivity of bismuthane imides toward the pinacol but also the pathway of the oxidation.

To obtain an insight into the structure of bismuthane imide **7**, an X-ray crystallographic study was performed. As shown in Figure 1, the bismuth atom is attached to the three carbon atoms C(1), C(12), and C(19) and one nitrogen atom N(1), with C−Bi−C bond angles of 112.0(5)−119.9(5)° and N(1)−Bi−C bond angles of 94.2(5)−107.8(5)°. The oxazoline nitrogen atom N(2) coordinates intramolecularly to the bismuth center from the opposite side of N(1) with a distance of 2.69(1) Å and an N(1)−Bi−N(2) bond angle of 163.5(4)°. The intramolecular distance between the bismuth and the N(2) atoms is longer than the sum of their covalent radii (2.16 Å) but shorter than that of their van der Waals radii (ca. 3.6 Å).[9] According to these findings, the geometry around the bismuth center can be regarded as a distorted-trigonal-bipyramidal structure (TBP). Since the coordination of N(2) to the bismuth center fixes the oxazoline ring, two *gem*-methyl groups on it are located above the plane made by two equatorial tolyl groups. From an open C(12)−Bi−C(19) side, one of the sulfonyl oxygen atoms O(1) coordinates to the bismuth at a distance of 2.97(1) Å, as shown in Figure 1; this value is intermediate between the sums of covalent radii (2.12 Å) and of van der Waals radii (ca. 3.5 Å) of bismuth and oxygen atoms.[9,10] The bismuth atom is located 0.49 Å above the plane made by the three carbon atoms C(1), C(12), and C(19).[11] The sum of three C−Bi−C bond angles (345.4°) lies between the predicted values of a TBP geometry (360°) and a tetrahedral geometry (328.5°). These observations are suggestive of some contribution of a tetrahedral nature to the total geometry of the bismuth center.

The most interesting feature of compound **7** is the Bi−N(1) bond length. The observed value (2.13(1) Å) falls in the range of the known Bi−N single-bond distances: 2.12(2)−2.28(2) Å for $(Ph_2N)_3Bi$,[12] 2.180(21)−2.189(18) Å for $(Me_2N)_3Bi$,[13] 2.14(2)−2.214(13) Å for $[(t\text{-}Bu_3C_6H_2)NH]_3Bi$,[14] 2.158(4)−2.174(5) Å for a cyclic amidobismuthane,[15] and 2.101(7)-2.237(7) Å for a cubic amidobismuthane.[16] A recent theoretical study on the electronic configuration of $H_3Bi{=}NH$ and $H_2Bi{-}NH_2$ at the MP2/DZ-d level estimated the lengths of the Bi═N and Bi−N bonds to be 1.997 and 2.133 Å, respectively.[17] Therefore, the Bi−N(1) bond in compound **7** can be regarded as a polarized single bond, $Bi^+{-}N^-$, rather than a double bond, Bi═N.

Coordination of the oxazoline nitrogen atom to the bismuth should play an important role in the stabilization of the polarized Bi−N bond, where the Bi, N(1), S, and O(1) atoms as well as all ring atoms of the oxazoline (C(7)−C(9), N(2), O(3)) are nearly coplanar with a mean deviation of 0.012 Å from the plane (C(1)−C(6)) defined by one of the benzene rings. These observations strongly suggest that the N(2)−Bi−N(1) linkage has a hypervalent bonding nature and that a charge on the Bi−N(imide) bond would be distributed over the array of N(2)−Bi−N(1)−S−O(1) atoms in a push−pull manner from the N(2) toward the O(1) end. The N(1)−S bond distance, 1.53(1) Å, is shorter than the sum of their covalent radii (1.74 Å), which suggests a double-bonding nature. This value is much shorter than those of ArI═NTs (1.611(2) and 1.595(4) Å), for which an S═N double-bond nature has also been proposed.[18] Therefore, it is reasonable to suppose that the structure C in Scheme 3 is the predominant resonance structure for imide **7**. In addition to this resonance between the imide and sulfonyl functions, the intramolecular coordination of the O(1) atom to the bismuth may also be effective for the stabilization of the Bi−N(imide) bond.

Scheme 3



X-ray crystallography and ^1H NMR spectroscopy support the conclusion that the structure of imide **7** is similar both in solution and in the solid state. A high-field shift (δ 0.68) of two *gem*-methyl groups on the oxazoline ring of imide **7** with respect to that (δ 1.13) of bismuthane **3** is probably due to the ring current effect of two tolyl groups, which have been found to partially eclipse the resonances of these methyl groups in the solid state. The *ortho* aromatic proton of the oxazoline-substituted phenyl group appears at δ 8.97, which is 0.99 ppm lower than that of compound **3**. A low-field shift of the *ortho* proton is caused by the deshielding effect of the nitrogen N(1) atom. These observations are indicative of the TBP structure of imide **7** in solution.

In conclusion, the oxazoline ring plays an important role as an intramolecularly coordinating ligand in the stability and reactivity of bismuthane imide **7**. The bismuth center of **7** has been found to possess the distorted-trigonal-bipyramidal geometry, in which the imide bond is best described as a polarized $Bi^+{-}N^-$ single bond.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of dry argon. THF and diethyl ether (Et_2O) were distilled from benzophenone ketyl under argon before use. 2-(4,4-Dimethyl-2-oxazolin-2-yl)phenyl bromide was prepared according to the reported procedure.[19] Commercially available reagents were used without further purification. Column chromatography was performed on silica gel (Wakogel, 200 mesh). Melting points were determined on a Yanagimoto hot-

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[9] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. Since the van der Waals radius of bismuth is not yet known, we postulated this value to be similar to that of antimony, 2.12 Å.

[10] If the coordination by oxygen O(1) is taken into consideration, the geometry around the bismuth center may be regarded as distorted octahedral.

[11] The observed distance between the bismuth atom and the corresponding plane is 0 Å for Ph_3BiCl_2 and 0.73 Å for $Ph_4Bi^+ClO_4^-$: Barton, D. H. R.; Charpiot, B.; Dau, E. T. H.; Motherwell, W. B.; Pascard, C.; Pichon, C. *Helv. Chim. Acta* **1984**, *67*, 586.

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stage apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. IR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer. Elemental analyses were performed at Microanalytical Laboratory, Institute of Chemical Research, Kyoto University.

[2-(4,4-Dimethyl-2-oxazolin-2-yl)phenyl]bis(4-methylphenyl)bismuthane (3). This compound was prepared according to a procedure recently established in our laboratory.[7b] To a solution of [2-(4,4-dimethyl-2-oxazolin-2-yl)phenyl]magnesium bromide **2**, prepared from the corresponding bromoarene (2.61 g, 10.3 mmol) and Mg (0.267 g, 11.0 mmol) in THF (20 mL), was added in one portion a solution of $Tol_2BiOTf{\cdot}2HMPA$[7a] (4.76 g, 5.3 mmol) in the same solvent (10 mL) at −20 °C under Ar. The resulting mixture was stirred at room temperature for 30 min and then poured into cold brine. The product was extracted with benzene (50 mL × 3). The combined extracts were dried and then concentrated to one-tenth of the original volume. Methanol (50 mL) was added and the mixture was allowed to stand at −15 °C to give bismuthane **3** as colorless crystals (1.89 g, 63%). Mp: 112−113 °C. ^{1}H NMR: δ 1.13 (s, 6H), 2.30 (s, 6H), 3.97 (s, 2H), 7.15 (d, $J_{AB} = 7.3$ Hz, 4H), 7.25 (dt, $J = 7.3$ and 1.7 Hz, 1H), 7.38 (dt, $J = 7.4$ and 1.7 Hz, 1H), 7.62 (d, $J_{AB} = 7.8$ Hz, 4H), 7.85 (dd, $J = 7.2$ and 1.5 Hz, 1H), 7.98 (dd, $J = 7.5$ and 1.7 Hz, 1H). ^{13}C NMR: δ 21.5, 28.4, 67.7, 79.0, 127.3, 129.4, 131.0, 133.0, 133.1, 136.5, 137.8, 139.4, 159.6, 160.2, 164.2. IR (KBr): 1644 (C=N), 1309, 1073, 1038, 795, 729, 683, 480 cm^{-1}. Anal. Calcd for $C_{25}H_{26}BiNO$: C, 53.10; H, 4.63; N, 2.48. Found: C, 53.18; H, 4.60; N, 2.51.

Chloro[2-(4,4-dimethyl-2-oxazolin-2-yl)phenyl](4-methylphenyl)bismuthane (4). Bismuthane **3** (1.70 g, 3.0 mmol) was passed through a silica gel column using $CHCl_3$ as the eluent. The chlorobismuthane **4** was obtained as colorless crystals (1.22 g, 80%). Mp: 184−186 °C. ^{1}H NMR: δ 1.13 (s, 3H), 1.43 (s, 3H), 2.24 (s, 3H), 4.24 (d, $J_{AB} = 8.5$ Hz, 1H), 4.30 (d, $J_{AB} = 8.5$ Hz, 1H), 7.27 (d, $J_{AB} = 7.4$ Hz, 2H), 7.56 (dt, $J = 7.5$ and 1.2 Hz, 1H), 7.86 (dt, $J = 7.5$ and 1.3 Hz, 1H), 7.98 (dd, $J = 7.2$ and 1.2 Hz, 1H), 8.01 (d, $J_{AB} = 7.9$ Hz, 2H), 9.10 (d, $J = 7.3$ Hz, 1H). ^{13}C NMR: δ 21.5, 28.1, 29.2, 67.1, 80.7, 127.9, 131.1, 131.9, 132.0, 135.9, 136.8, 137.4, 137.8, 175.0, 176.0, 179.4. IR (KBr): 1630 (C=N), 1375, 1327, 1088, 938, 793, 733, 478 cm^{-1}. Anal. Calcd for $C_{18}H_{19}BiClNO$: C, 42.41; H, 3.76; N, 2.75. Found: C, 42.43; H, 3.68; N, 2.70.

[2-(4,4-Dimethyl-2-oxazolin-2-yl)phenyl](4-methylphenyl)[*N*-(trifluoromethyl)sulfonamido]bismuthane (5). A solution of compound **4** (0.493 g, 0.97 mmol) in THF (20 mL) was added to a solution of $TfNH_2$ (0.144 g, 0.97 mmol) and *t*-BuOK (0.108 g, 0.97 mmol) in the same solvent (10 mL), and the resulting mixture was stirred at room temperature for 3 h. The solvent was evaporated to dryness, and the residue was extracted with CH_2Cl_2 (5 mL × 6). The combined extracts were concentrated to give compound **5** as crystals (0.603 g, 100%). Mp: 153−155 °C dec. ^{1}H NMR: δ 1.01 (s, 3H), 1.42 (s, 3H), 2.27 (s, 3H), 3.96 (broad s, 1H), 4.25 (d, $J_{AB} = 8.5$ Hz, 1H), 4.30 (d, $J_{AB} = 8.5$ Hz, 1H), 7.28 (d, $J_{AB} = 8.0$ Hz, 2H), 7.60 (dt, $J = 7.5$ and 1.1 Hz, 1H), 7.86 (d, $J_{AB} = 7.9$ Hz, 2H), 7.89 (dt, $J = 7.5$ and 1.4 Hz, 1H), 8.03 (dd, $J = 7.7$ and 1.4 Hz, 1H), 8.66 (dd, $J = 7.2$ and 1.0 Hz, 1H). ^{13}C NMR: δ 21.5, 28.0, 29.0, 67.1, 81.0, 117.1, 123.5, 128.3, 131.7, 132.2, 132.4, 136.1, 136.8, 138.5, 172.6, 176.4, 181.4. IR (KBr): 3279 (NH), 1632 (C=N), 1372 (SO_2), 1310, 1215, 1180 (SO_2), 1130, 1086, 976, 953, 729, 617 cm^{-1}. Anal. Calcd for $C_{19}H_{20}BiF_3N_2O_3S$: C, 36.67; H, 3.24; N, 4.50. Found: C, 36.02; H, 3.19; N, 4.35.

[2-(4,4-Dimethyl-2-oxazolin-2-yl)phenyl]bis(4-methylphenyl)bismuth Dichloride (6). A solution of bismuthane **3** (1.13 g, 2.0 mmol) in CH_2Cl_2 (10 mL) was added to a suspension of $PhICl_2$ (0.550 g, 2.0 mmol) in the same solvent (10 mL) at 5 °C. The resulting mixture was stirred at this temperature for 30 min and then concentrated under reduced pressure to one-fifth of the original volume. Dilution of the concentrate with ethanol (30 mL) gave compound **6** as yellow crystals (1.02 g, 80%). Mp: 187−189 °C dec. ^{1}H NMR: δ 0.96 (s, 6H), 2.40 (s, 6H), 4.15 (s, 2H), 7.43 (d, $J_{AB} = 7.7$ Hz, 4H), 7.53 (dt, $J = 7.4$ and 1.2 Hz, 1H), 7.66 (dt, $J = 7.8$ and 1.6 Hz, 1H), 7.79 (dd, $J = 7.8$ and 1.1 Hz, 1H), 8.07 (dd, $J = 7.4$ and 1.6 Hz, 1H), 8.5 (broad s, 4H). ^{13}C NMR: δ 21.3, 27.6, 67.9, 81.3, 124.6, 128.9, 129.8, 130.4, 131.0 (broad), 131.8, 134.7, 136.0 (broad), 140.9, 151.8 (broad), 162.2, 167.7. IR (KBr): 1649 (C=N), 1362, 1320, 1181, 1086, 1005, 992, 953, 808, 725, 475 cm^{-1}. Anal. Calcd for $C_{25}H_{26}BiCl_2NO$: C, 47.19; H, 4.12; N, 2.20. Found: C, 46.89; H, 4.02; N, 2.13.

Table 1. Crystallographic and Structure Solution Data for Imide 7

compd formula	$C_{26}H_{26}BiF_3N_2SO_3$
fw	712.54
cryst size, mm	0.32 × 0.10 × 0.10
cryst syst	monoclinic
space group	*C*2/*c*
a, Å	25.556(3)
b, Å	15.137(3)
c, Å	17.563(2)
β, deg	125.263(7)
V, Å^3	5547(1)
Z	8
D, g cm^{-3}	1.706
T, °C	23.0
radiation; λ, Å	Mo Kα; 0.710 69
μ(Mo Kα), cm^{-1}	64.69
$2\theta_{max}$, deg	55.0
no. of observns	6767 (6619 unique)
no. of rflns obsd	2652 ($I > 3.00\sigma(I)$)
no. of variables	325
rfln/param ratio	8.16
max peak in final diff map, e/Å^3	1.34
R	0.047
R_w	0.060
goodness of fit	1.10

[2-(4,4-Dimethyl-2-oxazolin-2-yl)phenyl]bis(4-methylphenyl)bismuthane [(Trifluoromethyl)sulfonyl]imide (7). Dichloride **6** (318 mg, 0.50 mmol) suspended in THF (15 mL) was added to a suspension of $TfNH_2$ (74.5 mg, 0.50 mmol) and *t*-BuOK (112 mg, 1.0 mmol) in the same solvent (10 mL), and the resulting mixture was stirred at room temperature for 1.5 h. The solvent was evaporated to dryness, and the residue was extracted with CH_2Cl_2 (10 mL × 4). The combined extracts were evaporated to one-tenth of the original volume, and Et_2O (10 mL) was added to the concentrate. The mixture was stood at −15 °C to give the imide **7** as a colorless solid (320 mg, 90%). Mp: 188−190 °C dec. ^{1}H NMR: δ 0.68 (s, 6H), 2.38 (s, 6H), 4.10 (s, 2H), 7.36 (d, $J_{AB} = 8.3$ Hz, 4H), 7.76 (d, $J_{AB} = 8.1$ Hz, 4H), 7.74 (dt, $J = 7.7$ and 1.0 Hz, 1H), 7.96 (dt, $J = 7.7$ and 1.3 Hz, 1H), 8.12 (dd, $J = 7.6$ and 1.5 Hz, 1H), 8.97 (d, $J = 7.8$ Hz, 1H). ^{13}C NMR: δ 21.4, 27.2, 67.8, 81.1, 118.5, 125.0, 130.0, 131.8, 132.0, 133.8, 135.3, 137.6, 141.8, 144.6, 148.2, 164.1. IR (KBr): 1642 (C=N), 1370 (SO_2), 1254, 1204, 1159 (SO_2), 1113, 1090, 988, 793, 613, 478 cm^{-1}. Anal. Calcd for $C_{26}H_{26}BiF_3N_2O_3S$: C, 43.83; H, 3.68; N, 3.93. Found: C, 43.32; H, 3.62; N, 3.85.

Hydrolysis of Imide 7. The imide **7** (100 mg, 0.148 mmol) in ethanol (15 mL) was heated under reflux for 2 h to give a cloudy solution, which was filtered through a Celite bed. The filtrate was evaporated to give a brown solid residue (86 mg), which contained Tol_3Bi (0.073 mmol, 49%), amidobismuthane **5** (0.050 mmol, 34%), and 2-(4,4-dimethyl-2-oxazolin-2-yl)benzene (0.098 mmol, 66%). The yields were based on imide **7**, and the product ratio was estimated by ^{1}H NMR. After silica gel column chromatography using hexane−ethyl acetate (10:1) as the eluent, Tol_3Bi (36 mg, 0.074 mmol, 50%) was obtained.

Thermolysis of Imide 7. Imide **7** (409 mg, 0.574 mmol) was heated at 200 °C for 10 min under reduced pressure (1 mmHg) to form an orange solid, which was dissolved in CH_2-

Table 2. Selected Bond Lengths and Angles for Imide 7, with Estimated Standard Deviations in Parentheses

Bond Lengths (Å)			
Bi−N(1)	2.13(1)	Bi−C(1)	2.23(1)
Bi−C(12)	2.19(1)	Bi−C(19)	2.20(2)
S−O(1)	1.45(1)	S−O(2)	1.43(1)
S−N(1)	1.53(1)	Bi−N(2)	2.69(1)
Bi−O(1)	2.97(1)		
Bond Angles (deg)			
N(1)−Bi−C(1)	94.2(5)	N(1)−Bi−C(12)	107.8(5)
N(1)−Bi−C(19)	105.9(5)	C(1)−Bi−C(12)	113.4(5)
C(1)−Bi−C(19)	112.0(5)	C(12)−Bi−C(19)	119.9(5)
O(1)−S−O(2)	116.7(7)	O(1)−S−N(1)	114.3(7)
O(2)−S−N(1)	114.4(7)	O(1)−S−C(26)	100.4(9)
O(2)−S−C(26)	102.5(9)	N(1)−S−C(26)	106.1(8)
Bi−N(1)−S	111.0(6)	C(1)−Bi−N(2)	69.3(5)
C(12)−Bi−N(2)	106.0(3)	C(19)−Bi−N(2)	82.1(5)
N(1)−Bi−N(2)	163.5(4)		

Cl_2 (30 mL); this solution was filtered through a Celite bed to remove insoluble materials. The filtrate was evaporated to give a brown residue (359 mg), which was revealed by ^1H NMR, using dibenzyl as an internal standard, to contain 62% (0.358 mmol) of amidobismuthane **5**.

NMR Monitoring of the Oxidation of Benzopinacol with Imide 7. Imide **7** (43 mg, 0.060 mmol), benzopinacol (20 mg, 0.055 mmol), and dibenzyl (20 mg, 0.11 mmol) were dissolved in $CDCl_3$ (0.7 mL), and the reaction was monitored by ^1H NMR at 25 °C. After 1 h the starting materials remained unchanged. After 12 h, imide **7** (27%), benzopinacol (32%), and amidobismuthane **5** (63%) had been formed. After 24 h, benzopinacol was consumed, and imide **7** (4%), amidobismuthane **5** (0.053 mmol, 89%), toluene (0.054 mmol, 45%), and benzophenone (0.108 mmol, 98%) were obtained. The yields were estimated by NMR spectroscopy, using dibenzyl as an internal standard.

X-ray Crystallography. Crystallographic data and details of the data collection procedures and structure refinement for imide **7** are presented in Table 1. Data were recorded on a Rigaku AFC7S diffractometer, with graphite-monochromated Mo Kα radiation, using the $\omega-2\theta$ scan technique. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects. No decay correction was applied. Structure solution and refinement were carried out by use of the Patterson method (DIRDIF92 PATTY)[20] and full-matrix least squares. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Selected intramolecular distances and angles are summarized in Table 2. Further details of the crystal structure investigation have been deposited at Cambridge Crystallographic Data Centre (CCDC), Cambridge, U.K.

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Supporting Information Available: Tables of X-ray data, atomic coordinates and thermal parameters, and bond distances and angles (15 pages). Ordering information is given on any current masthead page.

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