

Synthesis and Reactions of Some New Heterocyclic Bismuth-(III) and -(V) Compounds. 5,10-Dihydrodibenzo[*b,e*]bismine and Related Systems

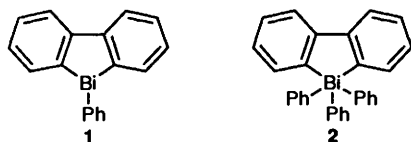
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New heterocyclic bismuth(III) compounds, 5-(4'-methylphenyl)-5,10-dihydrodibenzo[*b,e*]bismine **4**, its 10-oxa and 10-thia analogues **5**, **6** and **7** were synthesized and their reactions with benzoyl chloride and sulfonyl dichloride were investigated. Stable 10-alkynyl, alkenyl and alkyl-5-thiabismuth(III) compounds **13–15** and **19–21** were obtained from 10-halogeno derivatives **8** and **17**, but not from **3** and **16**. X-Ray structure analysis of compound **13** suggests a possible role for transannular interaction between the bismuth and heteroatom functions at the 5-position for the stabilization of labile chlorine–bismuth and aliphatic carbon–bismuth bonds in those systems.

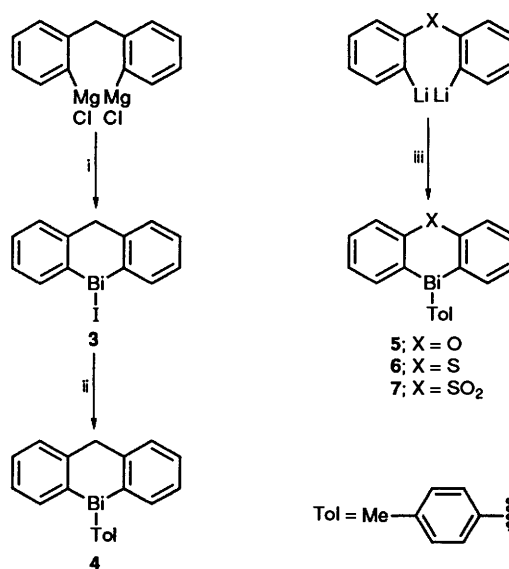
Only a few examples have hitherto been reported for the synthesis of heteroaromatic bismuth compounds. 5-Phenyldibenzo[*b,d*]bismole (biphenylenophenylbismuth) **1**, the first example of this class of compounds, was obtained by G. Wittig in 1964 as a stable, high melting solid (m.p. 167–168 °C) by the reaction of 2,2'-dilithiobiphenyl with diiodo(phenyl)bismuthine.¹ 9,9,9-Triphenyl- λ^5 -dibenzo[*b,d*]bismole (biphenylenetriphenylbismuth) **2** was subsequently isolated by D. Hellwinkel in 1968 as an orange-coloured solid by a similar reaction with dichlorotriphenylbismuth.² To the best of our knowledge, however, the chemistry of this class of compounds has been little explored. In the present work, we synthesized some new heterocyclic bismuth(III) compounds, *i.e.* 5-(4'-methylphenyl)-5,10-dihydrodibenzo[*b,e*]bismine **4** and its 10-oxa and 10-thia analogues (**5**, **6** and **7**), which were then transformed into a series of new heterocyclic bismuth-(III) and -(V) compounds bearing a variety of substituent group or groups on the bismuth atom. The stability of those compounds obtained was found to be greatly dependent on the functionality present at the 10-position (hetero atom) of the dihydrodibenzo[*b,e*]bismine ring.



Results and Discussion

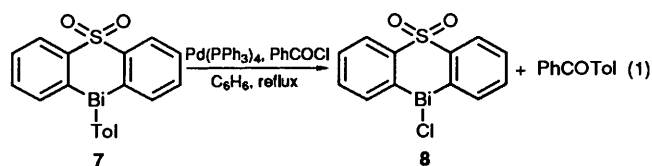
Two approaches were adopted for the synthesis of new heterocyclic bismuth(III) compounds **4–7**. As shown in Scheme 1, compounds **5–7** were synthesized in 40, 32 and 36% yield, respectively, by the reaction of dichloro(4-methylphenyl)bismuthine with the corresponding dilithio reagents, generated *in situ* by the *ortho*-dilithiation of starting aryl compounds or by the halogen–metal exchange reaction of the dibromo derivative.^{3–5} On the other hand, compound **4** was synthesized indirectly in 12% overall yield from the bismuth monoiodide **3** and 4-methylphenylmagnesium bromide to avoid difficulties involved in the separation of compound **4** by silica gel column chromatography. Owing to the ease of access to the starting material 2,2'-dichlorodiphenylmethane, the di-Grignard reagent was employed in the last case.⁶

Palladium(0)-catalysed Reaction with Benzoyl Chloride.—When compound **4** was heated with benzoyl chloride in benzene



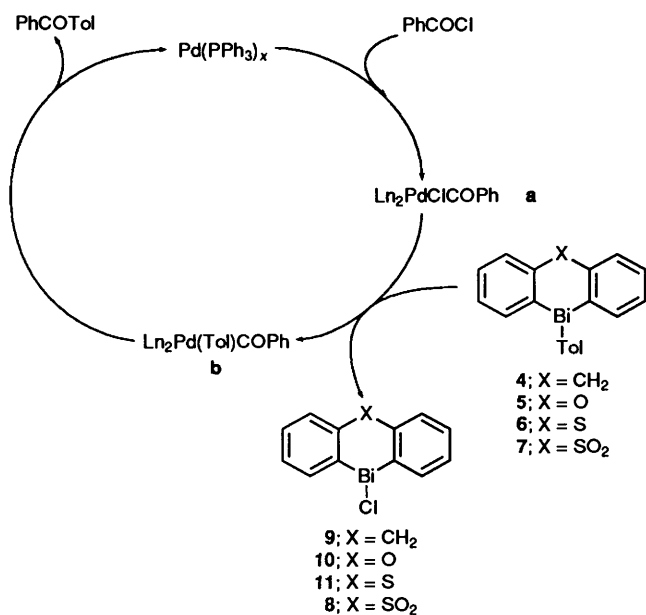
Scheme 1 Reagents: i, BiCl₃, KI, THF; ii, TolMgBr, THF; iii, TolBiCl₂, THF

for 7 h in the presence of Pd(PPh₃)₄ as catalyst, 4-methylbenzophenone was obtained in 80% yield together with a black deposit which apparently consisted of metallic components and resinous substances. Reactions of substrates **5** and **6** carried out under reflux conditions also led to similar results. When compound **5** was allowed to react with benzoyl chloride at room temperature, a bismuth-containing polymeric substance (m.p. > 300 °C) was formed as an insoluble white powder together with 4-methylbenzophenone.† In contrast, in the case of substrate **7**, the bismuth monochloride **8** was obtained in 86% isolated yield along with the ketone PhCOC₆H₄Me [eqn. (1)].



† Fragment peaks *m/z* 377 (9%, C₆H₄OC₆H₄Bi), 209 (100, Bi) and 168 (51, C₆H₄OC₆H₄) observed in the mass spectrum of this powder suggest that it is a hydrolytic degradation product of 10-chlorophenoxabismine **10**.

These results may be accounted for by a Pd^0 -catalysed mechanism as depicted in Scheme 2. The Pd^0 catalyst first undergoes oxidative addition with benzoyl chloride to afford intermediate **a**, which suffers ligand exchange with a heterocyclic bismuth compound 4–7 to give the corresponding bismuth monochloride 8–11. Reductive elimination of 4-methylbenzophenone from the intermediate **b** thus formed reproduces the Pd^0 catalyst. Owing to thermal instability and moisture sensitivity, compounds 9, 10 and 11 appear to decompose readily into bismuth-containing polymeric substances.



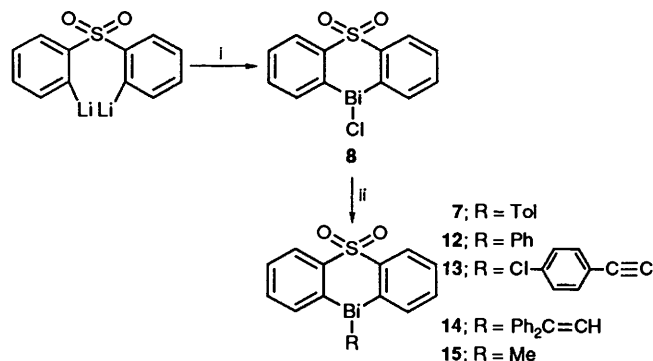
Scheme 2

It has been reported that triphenylbismuthine reacts with an excess of benzoyl chloride in the presence of a Pd^0 catalyst to give benzophenone and the bismuth(III) chloride.⁷ However, attempted reactions of our heterocyclic bismuth compounds under similar conditions resulted either in the formation of the bismuth(III) monochloride **8** together with 4-methylbenzophenone or in the decomposition to polymeric substances, no further cleavage leading to the bismuth(III) chloride being observed. This finding clearly indicates that the bidentate aryl ligand lowers the reactivity of the bismuth(III) monochloride **8–11** and resists further acylation. Unlike ordinary diarylchlorobismuthines which are quite moisture sensitive, compound **8** is a stable crystalline solid and can be handled without undergoing any change in the open air. This unexpected stability may be attributed to the transannular interaction between the bismuth and sulfonyl oxygen atoms, which stabilizes a labile bismuth–chlorine bond. An example of such interaction has been reported previously for the stabilization of some reactive organotellurenyl halogenides.⁸ Thus, compound **8** would be a useful intermediate for further transformation into other heterocyclic systems.

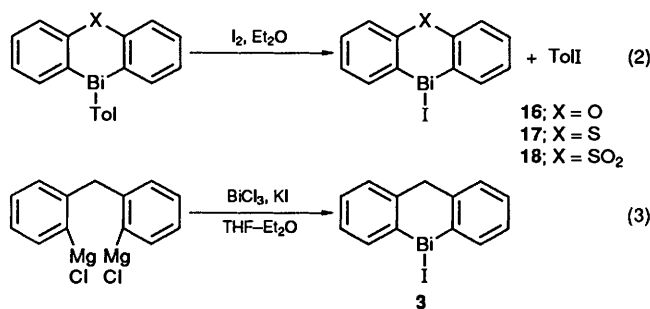
Synthesis and Transformations of the Bismuth(III) Monochloride 8.—Compound **8** was synthesized by the reaction of 2,2'-dilithiodiphenyl sulfone (1 mol equiv.) with bismuth(III) chloride (2 mol equiv.) in diethyl ether in 27% yield. Reaction of compound **8** with phenyllithium in tetrahydrofuran (THF) at -50°C afforded a mixture of triphenylbismuthine, diphenyl sulfone and the desired substitution product **12**.^{*} This drawback was overcome by the use of a Grignard reagent; compound **8** underwent substitution with 4-methylphenylmagnesium bromide quite smoothly at room temperature to give tolyl

compound **7** quantitatively even in the presence of excess of Grignard reagent. These results are rationalized by the difference in nucleophilicity between the two types of organometallic reagent; the more nucleophilic phenyllithium will effect further substitution with product **12** on the bismuth atom, leading eventually to triphenylbismuthine and 2,2'-dilithiodiphenyl sulfone.

Furthermore, compound **8** reacted with lithium arylacetylide, alkenyl and alkyl Grignard reagents to produce the corresponding substituted products **13–15** as stable crystalline solids in 86, 92 and 86% yield, respectively (Scheme 3). This type of bismuth moiety is known to be labile when present in acyclic structures due to the sensitivity of the bismuth–carbon bonds towards oxidation.^{9,10}

Scheme 3 Reagents: i, BiCl_3 , Et_2O ; ii, RM, THF

Synthesis and Transformations of the Bismuth(III) Monoiodides 3 and 16–18.—Compounds 5–7 easily underwent preferential fission of the Bi–C(Tol) bond by iodine to give bismuth(III) monoiodides **16–18** in 90, 75 and 92% yield, respectively, together with 4-iodotoluene [eqn. (2)]. Compound **3** could be directly obtained in 12% yield from the corresponding di-Grignard reagent and bismuth(III) chloride in the presence of potassium iodide [eqn. (3)].



For the sake of comparison with compound **13**, conversion of bismuth(III) monoiodides **3**, **16** and **17** into the corresponding alkynylbismuth(III) compounds was examined. Reaction of substrates **3** and **16** with lithium 4-chlorophenylacetylide led only to the decomposition of initial products with formation of bismuth-containing polymeric substances. However, a similar reaction with substrate **17** afforded a stable alkynylbismuth(III) compound, **19**, in 35% yield [eqn. (4)]. Furthermore, alkenyl- and even alkyl-bismuth compounds **20** and **21** were also obtained, in 58 and 35% yield, respectively, as stable crystalline solids from the reaction with the corresponding Grignard reagent. These results suggest that some stabilizing interaction

* Formation of triphenylbismuthine and diphenyl sulfone was confirmed by direct comparison with authentic samples.

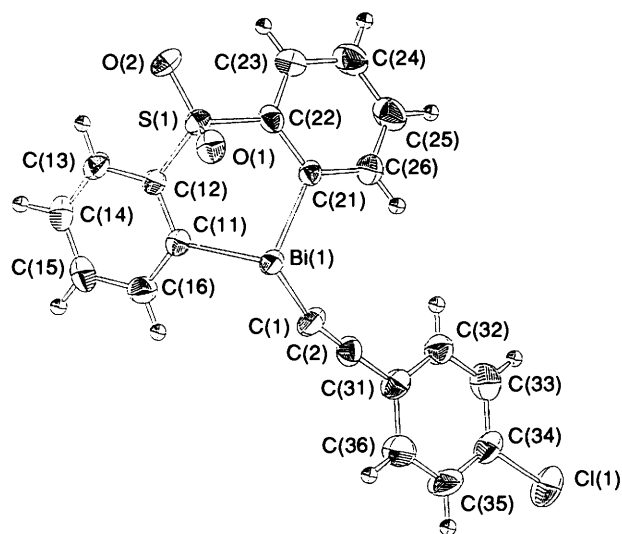
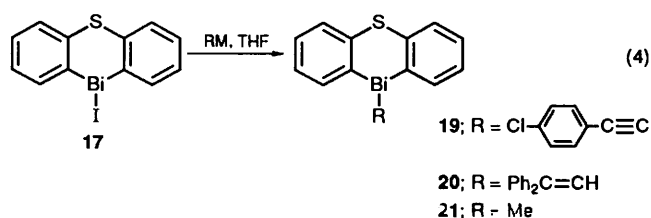


Fig. 1a An ORTEP²² perspective view of compound 13 with the atomic numbering scheme

as observed in the case of compounds 13–15 may also be operating for the generation of the unique stability of products 19–21.



X-Ray Structure Analysis of Compound 13.—In order to know the reason why compound 13 possesses a uniquely stable ring structure, we carried out an X-ray analysis on this compound. As shown in Fig. 1b, the bismuth atom has a pyramidal configuration with bond angles $C_{Ar}-Bi-C_{Ar}$, $87.0(3)^\circ$ and $C_{alkyne}-Bi-C_{Ar}$, $90.8(3)$ and $95.1(3)^\circ$, which are approximately comparable with those of $C_{Ph}-Bi-C_{Ph}$ of triphenylbismuthine, $92-96^\circ$.¹¹ The short length of bond $Bi-C_{alkyne}$ [$2.211(8)$ Å] as compared with those of $Bi-C_{Ar}$ [$2.283(8)$ and $2.272(7)$ Å] in the same molecule reflects the difference in electronic properties among each carbon atom attached to the bismuth atom. The most interesting feature of this molecule is the distance between the bismuth and sulfonyl oxygen atoms (see Table 2). The intramolecular distance $Bi(1)-O(1)$ is $2.979(7)$ Å, which is longer than the sum of the covalent radii (2.10 Å) but shorter than that of the Van der Waals radii (3.72 Å).^{12,13} This fact strongly supports the existence of a transannular interaction between both atoms. A similar $Bi-O$ transannular interaction was previously observed in an oxadithiobismocane system in which the distance between the two atoms is $2.97(1)$ Å.¹² In addition, the nearest intermolecular distance between the bismuth atom of one molecule and the sulfonyl oxygen atom of the other is $3.288(8)$ Å, suggesting the possibility that weak intermolecular interactions may also play a role between these two atoms. Thus it is readily understood that the bismuth atom is surrounded by two oxygen atoms capable of co-ordination in addition to three bonded carbon atoms in the solid structure and the additional co-ordinations by the sulfonyl oxygen atoms would greatly contribute to the special stabilization of labile bismuth–chlorine and bismuth–carbon bonds. A further interesting finding is a fairly marked bending of the acetylene carbon–bismuth bond angle $C(2)_{alkyne}-C(1)_{alkyne}-Bi$ $160.4(7)^\circ$. The reason is not clear

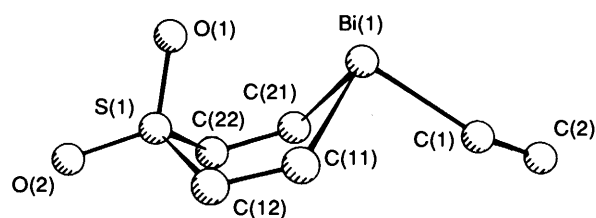
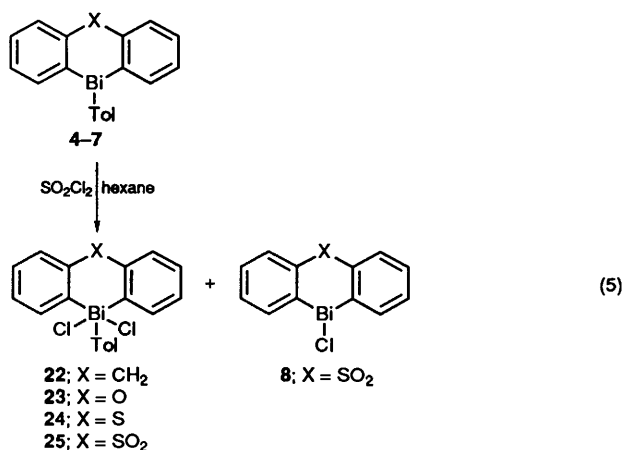


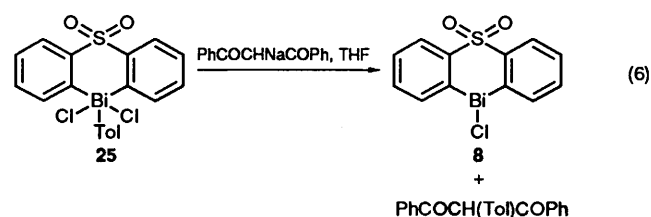
Fig. 1b A partial PLUTO²³ drawing of compound 13 around the bismuth centre

at present, but it might be explained by the presence of the acetylene bond in close proximity to the bismuth atom of the neighbouring molecule [$Bi-C(1)$ $3.523(8)$ and $Bi-C(2)$ 3.6728 Å].

Chlorination of Compounds 4–7 with Sulfuryl Dichloride.—In the presence of sulfuryl dichloride, the bismuth(III) substrates 4–7 readily underwent chlorination of the bismuth atom in hexane at room temperature to give the corresponding bismuth(V) dichlorides 22–25 as the respective products. The reaction proceeded quantitatively except for the case of substrate 7 where the bismuth(III) monochloride 8 was obtained in 36% yield, together with a 50% yield of the expected product 25 [eqn. (5)].



Compound 25 is a relatively stable, yellow, powdery substance, which slowly releases 4-chlorotoluene to form compound 8 under ambient conditions. When the bismuth(V) dichloride 25 was heated in dichloromethane for 5 min, the colour of the solution faded to colourless and the bismuth(III) compound 8 was obtained quantitatively along with 4-chlorotoluene. High oxidation states of certain organotellurium(IV) and organobismuth(V) compounds with Lewis base co-ordination have been reported readily to undergo reductive elimination to revert to the corresponding lower oxidation states.^{8,14} Thus a triaryldichlorobismuth(V) can serve as an excellent arylating reagent for a variety of carbon, nitrogen and oxygen nucleophiles.¹⁵ As expected, reaction of compound 25 with the sodium salt of dibenzoylmethane gave compound 8 and 2-(4'-methylphenyl)-1,3-diphenylpropane-1,3-dione in 74 and 76% yield, respectively [eqn. (6)].



Of three aryl groups attached to the bismuth atom, only the tolyl group participated in the reaction, reflecting the high stability of the ring structure formed by the co-ordination of the bidentate diarylsulfonyl grouping. A similar tendency was also confirmed in the reaction with iodine. Therefore, it became apparent that the introduction of a hetero functional group capable of interacting with the bismuth atom at an appropriate ring position would lead to heterocyclic bismuth-(III) and -(V) compounds of unique stability as well as interesting chemical reactivity.

Experimental

General Experimental Details.—All reactions were carried out under argon unless otherwise noted. Tetrahydrofuran and diethyl ether were distilled under argon from calcium hydride and sodium benzophenone ketyl, respectively, before use. Benzene was distilled from calcium hydride and stored over 4 Å molecular sieves. Butyllithium was titrated against diphenylacetic acid. TLC was performed by using Merck precoated silica gel sheets 60F-254. Silica gel (Wakogel) of the size 200 mesh was used for column chromatography. Commercially available bismuth(III) chloride was purified by refluxing with thionyl dichloride. All m.p.s were determined on a Yanagimoto hot-stage apparatus and are uncorrected. ¹H NMR spectra were recorded on a Varian Gemini-200 (200 MHz) or JEOL JMN-GX400 (400 MHz) spectrometer for solutions in CDCl₃ with tetramethylsilane as internal standard. Coupling constants *J* are given in Hz. IR spectra were obtained on a SHIMADZU FTIR-8100 spectrometer. Mass spectra were determined on a SHIMADZU GCMS-QP2000A spectrometer at an ionization potential of 70 eV. Elemental analyses were performed at Microanalytical Laboratory, Institute for Chemical Research, Kyoto University.

5-Iodo-5,10-dihydrodibenzo[b,e]bismine 3.—Preparation of the starting di-Grignard reagent was performed according to the procedure reported by T. C. Bedard.⁶ Activated magnesium was prepared by the refluxing of powdered anhydrous MgCl₂ (2.6 g, 27 mmol), potassium metal (1.8 g, 46 mmol) and potassium iodide (3.3 g, 20 mmol) in THF (30 cm³) for 2 h. To the resulting black suspension was added dropwise a solution of 2,2'-dichlorodiphenylmethane (2.4 g, 10 mmol) in the same solvent (10 cm³) and the mixture was refluxed for an additional 1 h. The solution of di-Grignard reagent was cooled to -20 °C and added dropwise to a solution of bismuth(III) chloride (3.2 g, 10 mmol) in diethyl ether (30 cm³) cooled to -50 °C. After being stirred for 10 h, during which time the temperature was gradually raised to 0 °C, the mixture was poured into cold brine (100 cm³) and ethyl acetate (100 cm³) was added. After insoluble polymeric substances had been filtered off, the organic layer was separated and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure to leave a yellow residue, which was recrystallized from hexane-CH₂Cl₂ (1:1) to afford the iodide **3** as yellow crystals (602 mg, 12%), m.p. 195–200 °C (decomp.); δ_H(200 MHz) 4.32 (2 H, s, CH₂), 7.26–7.40 (4 H, m, ArH), 7.89 (2 H, dd, *J* 1.6 and 7.0, ArH) and 8.28 (2 H, dd, *J* 1.8 and 6.9, ArH); ν_{max}(KBr)/cm⁻¹ 1430, 1420, 740, 620 and 420; *m/z* 375 (11%, M - I), 336 (11, BiI), 209 (100, Bi) and 166 (92, M - BiI) (Found: C, 31.1; H, 2.2. C₁₃H₁₀BiI requires C, 31.1; H, 2.0%).

5-(4'-Methylphenyl)-5,10-dihydrodibenzo[b,e]bismine 4.—To a solution of the iodide **3** (351 mg, 0.7 mmol) in THF (5 cm³) at 0 °C was added a solution of 4-methylphenylmagnesium bromide (~1.5 mmol) in the same solvent (3 cm³). After being stirred for 10 min at this temperature, the mixture was quenched by the addition of brine (5 cm³) and extracted with ethyl acetate

(20 cm³ × 3). The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure to afford a yellow, oily residue, recrystallization of which from MeOH-C₆H₆ (5:1) gave compound **4** as crystals (316 mg, 97%), m.p. 98–101 °C; δ_H 2.29 (3 H, s, Me), 3.85 (1 H, d, *J*_{AB} 14.7, 10-H), 4.01 (1 H, d, *J*_{AB} 14.7, 10-H), 7.09–7.27 (6 H, m, ArH), 7.56–7.65 (4 H, m, ArH) and 7.78–7.82 (2 H, dd, *J* 1.8 and 6.7, ArH); ν_{max}(KBr)/cm⁻¹ 1490, 1450, 1430, 1190, 1110, 1010, 820, 800, 740, 620, 480 and 430; *m/z* 300 (80%, BiC₆H₄CH₃), 209 (100, Bi) and 166 (61, M - BiC₆H₄CH₃) (Found: C, 52.0; H, 3.8. C₂₀H₁₇Bi requires C, 51.5; H, 3.7%).

10-(4'-Methylphenyl)phenoxabismine 5.—Dichloro-(4-methylphenyl)bismuthine (3.78 g, 10.2 mmol) was prepared as an insoluble yellow powder by ligand exchange between tris(4-methylphenyl)bismuthine (1.61 g, 3.33 mmol) and bismuth(III) chloride (2.15 g, 6.8 mmol) in diethyl ether (10 cm³) for 1 h at room temperature and was used *in situ* in the next step as a homogeneous diethyl ether-THF solution.

To a solution of 2,2'-dilithiodiphenyl ether³ generated from diphenyl ether (1.7 g, 10 mmol) and butyllithium (25 cm³) in diethyl ether-THF (100 cm³; 1:1) cooled to -70 °C was added dropwise a solution of dichloro(4-methylphenyl)bismuthine (3.78 g, 10.2 mmol) in diethyl ether-THF (30 cm³; 1:2) and the resulting mixture was stirred for 10 h, during which time the temperature was gradually raised to 0 °C. The reaction mixture was then poured into cold brine (100 cm³) and extracted with ethyl acetate (50 cm³ × 3). After an insoluble bismuth-containing polymeric substance had been filtered off, the organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to leave a yellow oily residue. Purification by silica gel column chromatography with hexane-ethyl acetate (5:1) as eluent afforded pure product **5** as crystals (1.87 g, 40%), m.p. 112–115 °C (from MeOH); δ_H 2.25 (3 H, s, Me), 7.05 (2 H, dt, *J* 1.2 and 7.3, OArH), 7.10 (2 H, d, *J*_{AB} 7.9, MeArH), 7.27 (2 H, dt, *J* 1.8 and 8.1, OArH), 7.61 (2 H, dd, *J* 1.2 and 8.0, OArH), 7.64 (2 H, d, *J*_{AB}, 7.9, MeArH) and 7.77 (2 H, dd, *J* 1.8 and 7.2, OArH); ν_{max}(KBr)/cm⁻¹ 1570, 1420, 1290, 1280, 1260, 1220, 1110, 890, 790, 750 and 470; *m/z* 468 (M⁺, 4%), 377 (4, M - C₆H₄CH₃), 300 (11, BiC₆H₄CH₃), 259 (3, M - Bi) and 209 (100, Bi) (Found: C, 48.8; H, 3.1. C₁₉H₁₅BiO requires C, 48.7; H, 3.1%).

10-(4'-Methylphenyl)phenothiabismine 6.—To a solution of 2,2'-dilithiodiphenyl sulfide,⁴ generated from 2,2'-dibromodiphenyl sulfide (3.42 g, 10 mmol) and butyllithium (25 mmol) in diethyl ether (100 cm³) at -70 °C was added dropwise a solution of dichloro(4-methylphenyl)bismuthine (3.78 g, 10.2 mmol) in diethyl ether-THF (30 cm³; 1:2) and the resulting mixture was stirred for 10 h, during which time the temperature was gradually raised to 0 °C. Usual extractive work-up with ethyl acetate, followed by purification by silica gel column chromatography with hexane-ethyl acetate (5:1) as eluent, afforded pure product **6** as crystals (1.55 g, 32%), m.p. 106–108 °C (from MeOH-C₆H₆; 5:1); δ_H 2.32 (3 H, s, Me), 7.11–7.16 (4 H, m, SArH), 7.19 (2 H, d, *J*_{AB} 7.9 MeArH), 7.60–7.64 (2 H, m, SArH), 7.77 (2 H, d, *J*_{AB} 7.9, MeArH) and 7.86–7.90 (2 H, m, SArH); ν_{max}(KBr)/cm⁻¹ 1440, 1240, 1180, 1090, 1060, 1030, 1010, 790, 760, 740, 720, 710, 570, 530, 480, 470 and 450; *m/z* 484 (M⁺, 89%), 300 (82, BiC₆H₄CH₃), 209 (100, Bi) and 184 (32, M - BiC₆H₄CH₃) (Found: C, 47.3; H, 3.1. C₁₉H₁₅BiS requires C, 47.1; H, 3.1%).

10-(4'-Methylphenyl)phenothiabismine 5,5-Dioxide 7.—To a solution of 2,2'-dilithiodiphenyl sulfone,⁵ generated from diphenyl sulfone (2.18 g, 10 mmol) and butyllithium (20 mmol) in diethyl ether (100 cm³), at -70 °C, was added dropwise a solution of dichloro(4-methylphenyl)bismuthine (3.78 g, 10.2

mmol) in diethyl ether-THF (30 cm³; 1:2) and the resulting mixture was stirred for 10 h, during which time the temperature was raised to 0 °C. Usual work-up as described above afforded pure *product 7* as crystals (1.86 g, 36%), m.p. 212–215 °C (from MeOH-C₆H₆; 5:1); δ_{H} 2.34 (3 H, s, Me), 7.24 (2 H, d, J_{AB} 8.0 MeArH), 7.29–7.44 (4 H, m, SO₂ArH), 7.65 (2 H, d, J_{AB} 8.0, MeArH), 7.87 (2 H, dd, J 1.6 and 6.8, SO₂ArH) and 8.38 (2 H, dd, J 1.8 and 7.2, SO₂ArH); ν_{max} (KBr)/cm⁻¹ 1450, 1440, 1430, 1300, 1280, 1250, 1080, 790, 770, 740, 720, 580, 560 and 470; m/z 425 (50%, M - C₆H₄CH₃), 300 (3, BiC₆H₄CH₃) and 209 (100, Bi) (Found: C, 44.1; H, 3.0. C₁₉H₁₅BiO₂S requires C, 44.2; H, 2.9%).

Pd⁰-Catalysed Reaction of Compound 4 with Benzoyl Chloride.—A mixture of compound **4** (326 mg, 0.7 mmol), benzoyl chloride (140 mg, 1 mmol) and benzene (5 cm³) was heated under reflux for 4 h in the presence of tetrakis(triphenylphosphine)palladium (81 mg, 0.07 mmol). An insoluble, brown, tarry matter was formed as the reaction proceeded. The reaction mixture was extracted with benzene (30 cm³) and the extract was concentrated under reduced pressure to give a yellow, oily residue, purification of which by silica gel column chromatography with hexane-ethyl acetate (5:1) as eluent gave 4-methylbenzophenone as crystals (110 mg, 80%), m.p. 57–58 °C (lit.^{1,6} 59.5 °C).

Pd⁰-Catalysed Reaction of Compound 5 with Benzoyl Chloride.—A mixture of compound **5** (468 mg, 1 mmol), benzoyl chloride (196 mg, 1.4 mmol) and benzene (5 cm³) was heated under reflux for 5 h in the presence of the Pd⁰ catalyst (115 mg, 0.1 mmol). An insoluble, brown, tarry matter was formed during the reaction. Usual extractive work-up with benzene, followed by purification by silica gel column chromatography with hexane-ethyl acetate (5:1) as eluent, afforded 4-methylbenzophenone as crystals (140 mg, 72%), m.p. 57–58 °C.

Pd⁰-Catalysed Reaction of Compound 6 with Benzoyl Chloride.—A mixture of compound **6** (482 mg, 1 mmol), benzoyl chloride (196 mg, 1.4 mmol) and benzene (5 cm³) was heated under reflux for 4 h in the presence of the Pd⁰ catalyst (115 mg, 0.1 mmol). A brown, tarry matter separated during the reaction. Work-up as described above afforded 4-methylbenzophenone as crystals (147 mg, 75%), m.p. 56–57 °C.

Pd⁰-Catalysed Reaction of Compound 7 with Benzoyl Chloride.—A mixture of compound **7** (516 mg, 1 mmol), benzoyl chloride (196 mg, 1.4 mmol) and benzene (5 cm³) was heated under reflux for 8 h in the presence of the Pd⁰ catalyst (115 mg, 0.1 mmol). The resulting solution was concentrated under reduced pressure to give a yellow, oily residue, purification of which by silica gel column chromatography with hexane-ethyl acetate (5:1) as eluent gave 10-chlorophenothiabismine 5,5-dioxide **8** and 4-methylbenzophenone. Compound **8** (396 mg, 86%) had m.p. 222–225 °C (from hexane-ethyl acetate; 5:1); δ_{H} 7.47 (2 H, dt, J 1.0 and 7.7), 7.72 (2 H, dt, J 1.3 and 7.6), 8.34 (2 H, dd, J 1.5 and 7.7) and 8.83 (2 H, dd, J 0.9 and 7.9); ν_{max} (KBr)/cm⁻¹ 1295, 1250, 1140, 1130, 1110, 760, 740, 590, 570 and 460; m/z 462 (1%, M + 2), 460 (M⁺, 3), 425 (13, M - Cl), 246 (17, BiCl) 244 (52, BiCl) and 209 (100, Bi) (Found: C, 30.8; H, 1.7. C₂₁H₈BiClO₂S requires C, 31.3; H, 1.75%). 4-Methylbenzophenone (110 mg, 80%) had m.p. 57–58 °C.

10-Chlorophenothiabismine 5,5-Dioxide 8.—To a well stirred suspension of 2,2'-dilithiodiphenyl sulfone⁵ generated from diphenyl sulfone (2.18 g, 10 mmol) and butyllithium (20 mmol) in diethyl ether (100 cm³) cooled to -70 °C was added dropwise

a solution of bismuth(III) chloride (6.31 g, 20 mmol) in the same solvent (40 cm³) and the resulting mixture was stirred for 10 h, during which time the temperature was gradually raised to 0 °C. The mixture was poured into cold brine (100 cm³) and ethyl acetate (150 cm³) was added. After insoluble polymeric substances had been filtered off, the organic layer was separated and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure to leave a yellow, oily residue, which was purified by silica gel column chromatography with hexane-ethyl acetate (5:1) as eluent to afford pure *product 8* as crystals (1.24 g, 27%), m.p. 222–225 °C (from hexane-ethyl acetate; 5:1); identical with the authentic sample obtained by the independent route (see above).

Reaction of Compound 8 with 4-Methylphenylmagnesium Bromide.—To a solution of compound **8** (460 mg, 1 mmol) in THF (10 cm³) was added a solution of 4-methylphenylmagnesium bromide (~1.5 mmol) in the same solvent (5 cm³). After being stirred for 10 min at room temperature, the mixture was quenched by the addition of brine (5 cm³) and extracted with ethyl acetate (20 cm³ × 3). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to leave an oily residue, which was recrystallized from MeOH-C₆H₆ (5:1) to give pure *product 7* as crystals (516 mg, 100%), m.p. 212–215 °C; identical with the authentic sample obtained by the independent route above.

10-(4'-Chlorophenylethynyl)phenothiabismine 5,5-Dioxide 13.—Lithium 4-chlorophenylacetylide was generated from the corresponding acetylene (150 mg, 1.1 mmol) and butyllithium (1.1 mmol) in THF at -30 °C and the resulting solution was added dropwise to a solution of compound **8** (460 mg, 1 mmol) in THF (10 cm³) at -50 °C. After being stirred for 2 h, during which the temperature was gradually raised to 0 °C, the mixture was quenched by the addition of brine (5 cm³) and extracted with ethyl acetate (20 cm³ × 3). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to leave an oily residue, which was recrystallized from hexane-CH₂Cl₂ (5:1) to give pure *product 13* as crystals (480 mg, 86%), m.p. 229–233 °C (decomp.); δ_{H} 7.27 (2 H, d, J_{AB} 8.5, ClArH), 7.38 (2 H, d, J_{AB} 8.5, ClArH), 7.43 (2 H, dt, J 1.4 and 7.3, SO₂ArH), 7.53 (2 H, dt, J 1.8 and 7.3, SO₂ArH), 8.33 (2 H, dd, J 1.5 and 8.9, SO₂ArH) and 8.72 (2 H, dd, J 1.4 and 7.1, SO₂ArH); ν_{max} (KBr)/cm⁻¹ 2100, 1485, 1300, 1290, 1200, 1090, 1010, 830, 770, 740, 640, 590 and 570; m/z 562 (1%, M + 2), 560 (M⁺, 4), 425 (10, M - Cl), 344 (53, BiCl) and 209 (100, Bi) (Found: C, 42.3; H, 2.2. C₂₀H₁₂BiClO₂S requires C, 42.8; H, 2.2%).

10-(2,2'-Diphenylvinyl)phenothiabismine 5,5-Dioxide 14.—To a solution of compound **8** (460 mg, 1 mmol) in THF (10 cm³) at 0 °C was added a solution of 2,2-diphenylvinylmagnesium bromide (~1.5 mmol) in the same solvent (5 cm³), and the mixture was stirred for 10 min. Usual work-up, followed by recrystallization from hexane-CH₂Cl₂ (5:1), afforded *compound 14* as crystals (556 mg, 92%), m.p. 218–220 °C; δ_{H} 7.30 (5 H, s, Ph), 7.39–7.45 (4 H, m, SO₂ArH), 7.50 (5 H, s, Ph), 8.19–8.23 (2 H, m, SO₂ArH), 8.31–8.36 (2 H, m, SO₂ArH) and 9.04 (1 H, s, BiCHCPh₂); ν_{max} (KBr)/cm⁻¹ 1560, 1490, 1480, 1440, 1300, 1280, 1250, 1150, 1090, 1070, 1010, 810, 760, 740, 700, 590, 570, 520 and 460; m/z 425 (43%, M - CHCPh₂) and 209 (100, Bi) (Found: C, 51.7; H, 3.3. C₂₆H₁₉BiO₂S requires C, 51.7; H, 3.2%).

10-Methylphenothiabismine 5,5-Dioxide 15.—To a solution of compound **8** (460 mg, 1 mmol) in THF (10 cm³) at 0 °C was added a solution of methylmagnesium iodide (~1.5 mmol) in diethyl ether (5 cm³) and the mixture was stirred for 10 min. Usual work-up, followed by recrystallization from MeOH-

C_6H_6 (5:1), afforded *compound 15* as crystals (378 mg, 86%), m.p. 180–183 °C; δ_H 1.41 (3 H, s, Me), 7.33–7.47 (4 H, m, ArH), 8.02–8.07 (2 H, m, ArH) and 8.28–8.32 (2 H, m, ArH); $\nu_{max}(KBr)/cm^{-1}$ 1290, 1250, 1150, 590 and 570; m/z 425 (40%, M – CH₃) and 209 (100, Bi) (Found: C, 35.4; H, 2.5. C₁₃H₁₁BiO₂S requires C, 35.5; H, 2.5%).

10-Iodophenoxabismine 16.—To a suspension of compound **5** (468 mg, 1 mmol) in diethyl ether (5 cm³) was added dropwise a solution of iodine (254 mg, 1 mmol) in the same solvent (5 cm³) under ambient conditions. The precipitated yellow powder was filtered off, washed with diethyl ether (5 cm³), and recrystallized from hexane–CH₂Cl₂ (5:1) to give pure *product 16* as pale yellow crystals (453 mg, 90%), m.p. 150–155 °C (decomp.); δ_H 7.22 (2 H, dt, *J* 1.3 and 7.2), 7.36 (2 H, dt, *J* 1.8 and 8.1), 7.90 (2 H, dd, *J* 1.3 and 8.0) and 8.38 (2 H, dd, *J* 1.8 and 7.3); $\nu_{max}(KBr)/cm^{-1}$ 1570, 1450, 1430, 1420, 1320, 1260, 1210, 1180, 1110, 890, 860, 790, 750 and 430; m/z 504 (M⁺, 1%), 377 (40, M – I), 336 (7, BiI), 209 (100, Bi) and 168 (14, M – BiI) (Found: C, 28.3; H, 1.6. C₁₂H₈BiIO requires C, 28.6; H, 1.6%).

10-Iodophenothiabismine 17.—To a suspension of compound **6** (484 mg, 1 mmol) in diethyl ether (5 cm³) was added dropwise a solution of iodine (254 mg, 1 mmol) in the same solvent (5 cm³) under ambient conditions. Similar work-up as above, followed by recrystallization from hexane–CH₂Cl₂ (5:1), afforded *compound 17* as pale yellow crystals (390 mg, 75%), m.p. 187–190 °C; δ_H 7.28 (2 H, dt, *J* 1.4 and 7.4), 7.50 (2 H, dt, *J* 1.4 and 7.5), 7.83 (2 H, dd, *J* 1.5 and 7.8) and 8.99 (2 H, dd, *J* 1.0 and 7.4); $\nu_{max}(KBr)/cm^{-1}$ 1420, 750 and 440; m/z 393 (15%, M – I), 336 (10, BiI), 209 (100, Bi) and 184 (58, M – BiI) (Found: C, 28.0; H, 1.8. C₁₂H₈BiIS requires C, 27.7; H, 1.5%).

10-Iodophenothiabismine 5,5-Dioxide 18.—To a suspension of compound **7** (516 mg, 1 mmol) in diethyl ether (5 cm³) was added dropwise a solution of iodine (254 mg, 1 mmol) in the same solvent (5 cm³) under ambient conditions. Usual work-up, followed by recrystallization from hexane–CH₂Cl₂ (5:1), afforded *compound 18* as pale yellow crystals (508 mg, 92%), m.p. 277–280 °C; δ_H 7.48 (2 H, dt, *J* 1.2 and 7.5), 7.61 (2 H, dt, *J* 1.4 and 7.4), 8.30 (2 H, dd, *J* 1.3 and 7.6) and 9.22 (2 H, dd, *J* 1.0 and 7.3); $\nu_{max}(KBr)/cm^{-1}$ 1560, 1440, 1420, 1300, 1290, 1250, 1140, 1130, 1120, 1090, 1070, 1010, 590, 570, 510, 460 and 420; m/z 425 (44%, M – I), 336 (9, BiI) and 209 (100, Bi) (Found: C, 26.1; H, 1.5. C₁₂H₈BiIO₂S requires C, 26.1; H, 1.5%).

10-(4'-Chlorophenylethynyl)phenothiabismine 19.—To a solution of compound **17** (520 mg, 1 mmol) in THF (10 cm³) cooled to –50 °C was added dropwise a solution of lithium 4-chlorophenylacetylide (~1.1 mmol) in the same solvent (5 cm³) cooled to –30 °C and the mixture was stirred for 2 h, during which the temperature was gradually raised to 0 °C. Usual work-up with ethyl acetate, followed by recrystallization from hexane–CH₂Cl₂ (5:1), gave *compound 19* as crystals (185 mg, 35%), m.p. 153–156 °C; δ_H 7.18–7.32 (4 H, m), 7.33–7.45 (4 H, m), 7.88 (2 H, dd, *J* 1.5 and 7.1, SArH) and 8.47 (2 H, dd, *J* 1.2 and 7.3, SArH); $\nu_{max}(KBr)/cm^{-1}$ 1490, 1420, 1200, 1090, 1010, 830, 750, 640, 530 and 450; m/z 209 (100%, Bi), 184 (40, M – BiC₂C₆H₄Cl) and 136 (62, ClC₆H₄C₂H) (Found: C, 45.35; H, 2.3. C₂₀H₁₂BiClS requires C, 45.4; H, 2.3%).

10-(2',2'-Diphenylvinyl)phenothiabismine 20.—To a solution of compound **17** (520 mg, 1 mmol) in THF (10 cm³) at 0 °C was added dropwise a solution of 2,2-diphenylvinylmagnesium bromide (~1.5 mmol) in the same solvent (5 cm³) and the mixture was stirred for 5 min. Usual work-up, followed by

recrystallization from hexane–CH₂Cl₂ (5:1), afforded *compound 20* as crystals (331 mg, 58%), m.p. 149–152 °C; δ_H 7.16–7.48 (14 H, m), 7.89 (2 H, dd, *J* 1.7 and 7.1, SArH), 7.97 (2 H, dd, *J* 1.8 and 6.8, SArH) and 9.02 (1 H, s, BiCHCPh₂); $\nu_{max}(KBr)/cm^{-1}$ 1550, 1510, 1490, 1420, 750, 700, 680 and 640; m/z 572 (M⁺, 7%), 388 (12, BiCHCPh₂), 363 (31, M – Bi) and 209 (100, Bi) (Found: C, 54.9; H, 3.45. C₂₆H₁₉BiS requires C, 54.55; H, 3.35%).

10-Methylphenothiabismine 21.—To a solution of compound **17** (520 mg, 1 mmol) in THF (10 cm³) at 0 °C was added dropwise a solution of methylmagnesium iodide (~1.5 mmol) in diethyl ether (5 cm³) and the mixture was stirred for 5 min. Usual work-up, followed by recrystallization from MeOH–C₆H₆ (5:1), afforded *compound 21* as crystals (145 mg, 35%), m.p. 125–127 °C; δ_H 1.41 (3 H, s, Me), 7.09–7.24 (4 H, m, ArH) and 7.73–7.84 (4 H, m, ArH); $\nu_{max}(KBr)/cm^{-1}$ 1420, 1250, 1140, 1090, 1060, 1030, 1010, 980, 940, 860, 750, 720, 710, 530, 450 and 420; m/z 409 (19%, M + 1), 393 (18, M – CH₃), 209 (100, Bi) and 184 (23, M – BiCH₃) (Found: C, 38.4; H, 2.75. C₁₃H₁₁BiS requires C, 38.2; H, 2.7%).

5,5-Dichloro-5-(4'-methylphenyl)-5,10-dihydro-5 λ ⁵-dibenzo-[b,e]bismine 22.—To a suspension of compound **4** (326 mg, 0.7 mmol) in hexane (5 cm³) was added dropwise a solution of sulfuryl dichloride (135 mg, 1 mmol) in the same solvent (5 cm³) and the mixture was stirred for 2 h. The pale yellow, powdery deposit was filtered off, washed with hexane (5 cm³) and recrystallized to afford *compound 22* as pale yellow crystals (342 mg, 91%). Owing to its low stability in solution further purification could not be attempted; m.p. 167–171 °C (decomp.); δ_H 2.50 (3 H, s, Me), 4.76 (2 H, s, CH₂), 7.37–7.53 (4 H, m, CH₂ArH), 7.58 (2 H, d, *J*_{AB} 8.8, MeArH), 7.69 (2 H, d, *J* 7.2, CH₂ArH), 7.90 (2 H, d, *J* 7.5, CH₂ArH) and 8.67 (2 H, d, *J*_{AB} 8.8, MeArH); $\nu_{max}(KBr)/cm^{-1}$ 1460, 1440, 1180, 990, 790, 780, 750, 610, 470 and 430; m/z 410 (1%, M – CH₃C₆H₄Cl), 374 (6, M – CH₃C₆H₄Cl₂H), 300 (1, BiC₆H₄CH₃), 244 (4, BiCl), 209 (68, Bi) and 166 (100, C₆H₄CH₂C₆H₄).

10,10-Dichloro-10-(4'-methylphenyl)phenoxy-10 λ ⁵-bismine 23.—To a suspension of compound **5** (468 mg, 1 mmol) in hexane (5 cm³) was added dropwise a solution of sulfuryl dichloride (190 mg, 1.4 mmol) in the same solvent (5 cm³) and the mixture was stirred for 2 h. Usual work-up afforded *compound 23* as a pale yellow powder (500 mg, 93%). Owing to its instability in solution further purification was not possible; m.p. 134–137 °C (decomp.); δ_H 2.51 (3 H, s, Me), 7.31 (2 H, dt, *J* 1.3 and 7.3, OArH), 7.47 (2 H, dt, *J* 1.6 and 8.2, OArH), 7.56 (2 H, d, *J*_{AB} 8.7, MeArH), 7.73 (2 H, dd, *J* 1.4 and 8.1, OArH), 7.91 (2 H, dd, *J* 1.8 and 7.7, OArH) and 8.63 (2 H, d, *J*_{AB} 8.7, MeArH); $\nu_{max}(KBr)/cm^{-1}$ 1570, 1450, 1430, 1260, 1210, 1180, 990, 880, 790, 780, 750, 470 and 430; m/z 468 (1%, M – Cl₂), 377 (5, M – C₆H₄CH₃Cl₂), 300 (3, BiC₆H₄CH₃), 209 (100, Bi) and 168 (91, C₆H₄OC₆H₄).

10,10-Dichloro-10-(4'-methylphenyl)phenoxy-10 λ ⁵-bismine 24.—To a suspension of compound **6** (484 mg, 1 mmol) in hexane (5 cm³) was added dropwise a solution of sulfuryl dichloride (190 mg, 1.4 mmol) in the same solvent (5 cm³) and the mixture was stirred for 2 h. Usual work-up, followed by recrystallization from hexane–CH₂Cl₂ (5:1), afforded *compound 24* as pale yellow crystals (506 mg, 94%), m.p. 139–142 °C; δ_H 2.51 (3 H, s, Me), 7.35–7.50 (4 H, m, SArH), 7.59 (2 H, d, *J*_{AB} 8.7, MeArH), 7.86–7.93 (4 H, m, SArH) and 8.69 (2 H, d, *J*_{AB} 8.7, MeArH); $\nu_{max}(KBr)/cm^{-1}$ 1440, 1250, 990, 790, 750, 470 and 450; m/z 484 (8%, M – Cl₂), 393 (10, BiC₆H₄CH₃), 209 (100, Bi), 184 (89, C₆H₄SC₆H₄) and 126 (85, CH₃C₆H₄Cl) (Found: C, 41.0; H, 2.8. C₁₉H₁₅BiCl₂S requires C, 41.1; H, 2.7%).

Table 1 Positional parameters for compound **13** with estimated standard deviations in parentheses

Atom	x	y	z
Bi(1)	0.430 69(3)	0.021 20(2)	0.226 22(3)
Cl(1)	0.391 5(3)	-0.604 1(2)	0.760 6(3)
S(1)	0.189 8(2)	0.213 2(2)	-0.085 2(2)
O(1)	0.353 7(6)	0.189 9(4)	-0.056 0(6)
O(2)	0.083 6(6)	0.295 7(4)	-0.216 9(6)
C(1)	0.378 1(8)	-0.087 4(6)	0.388(1)
C(2)	0.379 3(8)	-0.171 7(6)	0.457(1)
C(11)	0.235 7(7)	0.187 2(6)	0.243 5(8)
C(12)	0.146 1(8)	0.257 1(6)	0.103 2(8)
C(13)	0.028 3(8)	0.361 1(6)	0.101 7(9)
C(14)	0.001 2(9)	0.398 1(6)	0.250(1)
C(15)	0.085 8(9)	0.331 2(7)	0.393(1)
C(16)	0.202 0(8)	0.224 2(7)	0.391 6(9)
C(21)	0.261 9(7)	-0.013 0(5)	0.004 3(7)
C(22)	0.165 1(8)	0.078 6(6)	-0.112 5(8)
C(23)	0.057 5(9)	0.065 0(7)	-0.250 3(9)
C(24)	0.044(1)	-0.041 8(8)	-0.274(1)
C(25)	0.138(1)	-0.134 3(8)	-0.158(1)
C(26)	0.245 3(9)	-0.119 5(6)	-0.020(1)
C(31)	0.376 9(8)	-0.274 1(6)	0.533 1(9)
C(32)	0.296 6(8)	-0.340 5(7)	0.442(1)
C(33)	0.299 8(9)	-0.441 5(7)	0.514(1)
C(34)	0.383 1(8)	-0.475 7(6)	0.673(1)
C(35)	0.462(1)	-0.410 9(8)	0.766(1)
C(36)	0.458(1)	-0.310 0(7)	0.696(1)

Table 2 Selected bond lengths (Å) and angles (°) for compound **13**, with estimated standard deviations in parentheses

Intramolecular distances		Bond angles	
Bi(1)–C(1)	2.211(8)	C(1)–Bi(1)–C(11)	95.1(3)
Bi(1)–C(11)	2.283(8)	C(1)–Bi(1)–C(21)	90.8(3)
Bi(1)–C(21)	2.272(7)	C(11)–Bi(1)–C(21)	87.0(3)
C(1)–C(2)	1.20(1)	Bi(1)–C(1)–C(2)	160.4(7)
S(1)–O(1)	1.456(6)	C(1)–C(2)–C(31)	177.7(8)
S(1)–O(2)	1.437(6)		
Bi(1)···O(1)	2.979(7)		
Intermolecular distances			
Bi(2)···O(1)	3.288(8)		
Bi(2)···C(1)	3.523(8)		
Bi(2)···C(2)	3.672(8)		

10,10-Dichloro-10-(4'-methylphenyl)phenothia-10λ⁵-bismine 5,5-Dioxide **25**.—To a suspension of compound **7** (516 mg, 1 mmol) in hexane (5 cm³) was added dropwise a solution of sulfuryl dichloride (190 mg, 1.4 mmol) in the same solvent (5 cm³) and the mixture was stirred for 3 h. The resulting pale yellow, powdery deposit was filtered off and washed with hexane (5 cm³). Purification by silica gel column chromatography with hexane–ethyl acetate (4:1) as eluent afforded compound **25** as a yellow viscous oil along with compound **8**. Recrystallization from hexane–ethyl acetate (5:1) afforded crude compound **25** as a yellow powder (294 mg, 50%). Owing to its instability in solution further purification was abandoned; m.p. 110–115 °C (decomp.); δ_H 2.44 (3 H, s, Me), 7.47 (2 H, d, J_{AB} 8.8, MeArH), 7.60 (2 H, t, J 7.0, SO₂ArH), 7.85 (2 H, dt, J 1.4 and 7.7, SO₂ArH), 8.23 (2 H, dd, J 1.2 and 7.5, SO₂ArH), 8.33 (2 H, d, J_{AB} 8.8, MeArH) and 8.76 (2 H, d, J 7.7, SO₂ArH); ν_{max}(KBr)/cm⁻¹ 1560, 1540, 1460, 1430, 1320, 1170, 1150, 1110, 980, 790, 770, 740, 710, 640, 580, 570, 520, 460 and 440; m/z 462 (1%), 460 (2, M – CH₃C₆H₄Cl), 244 (55, BiCl), 209 (100, Bi) and 126 (7, CH₃C₆H₄Cl); compound **8** (166 mg, 36%) had m.p. 222–225 °C (from hexane–ethyl acetate; 5:1); δ_H 7.47 (2 H, dt, J 1.0 and 7.7), 7.72 (2 H, dt, J 1.3 and 7.6), 8.34 (2 H, dd, J 1.5 and 7.7) and 8.83 (2 H, dd, J 0.9 and 7.9); ν_{max}(KBr)/cm⁻¹ 1295, 1250, 1140, 1130, 1110, 760, 740, 590, 570 and 460; m/z 562 (1%, M +

2), 560 (M⁺, 4), 425 (10, M – Cl), 344 (53, BiCl) and 209 (100, Bi).

Reaction of Compound 25 with the Sodium Salt of Dibenzoylmethane.—To a solution of compound **25** (587 mg, 1 mmol) in THF (10 cm³) at –50 °C was added dropwise a solution of the sodium salt of dibenzoylmethane generated from sodium hydride (44 mg, 1.1 mmol; 60%) and dibenzoylmethane (224 mg, 1 mmol) in the same solvent (10 cm³) and the solution was stirred for 2 h, during which the temperature was gradually raised to 0 °C. The resulting mixture was concentrated under reduced pressure and then extracted with ethyl acetate (20 cm³). Silica gel column chromatography of the extract with hexane–ethyl acetate (5:1) as the eluent afforded compound **8** and 2-(4'-methylphenyl)-1,3-diphenylpropane-1,3-dione. Compound **8** (340 mg, 74%) had m.p. 222–225 °C (from hexane–ethyl acetate; 5:1); 2-(4'-methylphenyl)-1,3-diphenylpropane-1,3-dione, m.p. 147–150 °C (from hexane–CH₂Cl₂; 10:1); δ_H(400 MHz) 2.32 (3 H, s, Me), 6.53 (1 H, s), 7.18 (2 H, d, J_{AB} 7.9), 7.27 (2 H, d, J_{AB} 7.9), 7.42 (4 H, t, J 7.3), 7.54 (2 H, t, J 7.3) and 7.97 (4 H, d, J 8.6); ν_{max}(KBr)/cm⁻¹ 3050, 1680, 1670, 1590, 1580, 1520, 1450, 1330, 1300, 1290, 1260, 1230, 1200, 1170 and 1010; m/z 314 (M⁺, 16%), 209 (5, M – PhCO), 105 (100, PhCO) and 77 (43, Ph).

X-Ray Crystallography of Compound 13.—A crystal of dimensions 0.200 × 0.070 × 0.200 mm was used for X-ray crystallography.

Crystal data: C₂₀H₁₂BiClO₂S, M = 560.81. Triclinic, space group *P* $\bar{1}$, *a* = 9.64(2), *b* = 12.35(2), *c* = 8.465(4) Å, α = 91.63(9), β = 105.39(9), γ = 69.7(1)°, *V* = 909(3) Å³, *Z* = 2, *D*_c = 2.048 g cm⁻³. Plates, μ(MoKα, λ = 0.710 69 Å) = 99.36 cm⁻¹. Intensity data were recorded on a Rigaku AFC5R diffractometer with graphite-monochromated Mo-Kα radiation and a 12 kW rotating anode generator using the ω–2θ scan technique to a maximum 2θ-value of 55.0°. Scans of (1.10 + 0.30 tanθ)° were made at a speed of 16.0 deg min⁻¹ (in ω). Of the 4417 reflections which were collected, 4169 were unique (*R*_{int} = 0.032). Data were corrected for Lorentz, polarization and absorption effects. The structure was solved by a combination of the Patterson method and direct methods.¹⁷ The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 3331 observed reflections [*I* > 3.00σ(*I*)] and 227 variable parameters and converged with unweighted and weighted agreement factors of *R* = 0.032 and *R*_w = 0.036. The weighting scheme, *w* = 1/σ²(*F*_o), was employed. Neutral atom-scattering factors were taken from Cromer and Waber.¹⁸ Anomalous dispersion effects were included in *F*_{calc}.¹⁹ The values for Δ*f*' and Δ*f*" were those of Cromer.²⁰ All calculations were performed on a VAX station 3200 computer using the TEXSAN²¹ crystallographic software package from the Molecular Structure Corporation. The ORTEP²² and PLUTO²³ programs were used to obtain Figs. 1a and 1b.*

Fractional atomic co-ordinates, and selected bond lengths and bond angles are given in Tables 1 and 2. Full details of crystal data, fractional atomic co-ordinates, bond lengths, bond angles, hydrogen co-ordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

* **Supplementary data** (see section 5.6.3, Instructions to Authors, in the January issue).

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