

Synthesis of Arylbismuth(III) Sulfonates from Triarylbismuth Compounds and Arenesulfonic Acids or Sulfur Trioxide

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Abstract

Reactions of triphenyl- and tri-*p*-tolyl-bismuth with the appropriate arenesulfonic acids give the diarylbismuth(III) sulfonates, R_2BiO_3SR' ($R, R' = Ph$ or $p-MeC_6H_4$). $(p-MeC_6H_4)_3Bi$ reacts with $PhSO_3H$ (mole ratio, 1:2) under more aggressive conditions to give impure $p-MeC_6H_4Bi(O_3SPh)_2$. From reactions of the bismuthines with sulfur trioxide, Ph_2BiO_3SPh (not $Ph_3Bi \cdot SO_3$ as previously indicated [1]) and a mixture of $(p-MeC_6H_4)_2BiO_3S-p-MeC_6H_4$ and $p-MeC_6H_4Bi(O_3S-p-MeC_6H_4)_2$ have been obtained. On prolonged standing, Ph_2BiO_3SR' ($R' = Ph$ or $p-MeC_6H_4$) compounds decompose into $BiO(O_3SR')$ and a small amount of triphenylbismuth.

Introduction

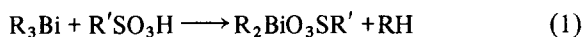
The product from the reaction of triphenylbismuth with sulfur trioxide has been formulated as the adduct $Ph_3Bi \cdot SO_3$ [1]. The most compelling evidence for this composition was the formation of triphenylbismuth and sulfuric acid on hydrolysis. However sulfur trioxide is known to insert into Group 4B metal–carbon bonds to give sulfonato complexes [2], and it has been shown that the product from the reaction of triphenylbismuth with sulfur dioxide, originally formulated as the adduct $Ph_3Bi \cdot 2SO_2$ [3], is actually $PhBi(O_2SPh)_2$ [4]. Authentic arylbismuth(III) sulfonates for comparison with products of reactions with sulfur trioxide are potentially available from reactions of triarylbismuth compounds with sulfonic acids, since we have recently shown that $R_nBi(O_2CR')_{3-n}$ ($n = 1, 2$) complexes can be prepared by reaction of triorgano-bismuthines with carboxylic acids [5, 6]. Accordingly, we now report a study of reactions of triphenyl- and tri-*p*-tolyl-bismuth with sulfonic acids and with sulfur trioxide.

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Results and Discussion

(a) Reactions with Sulfonic Acids

The arylbismuth(III) sulfonates R_2BiO_3SR' ($R, R' = Ph$ or $p-MeC_6H_4$) have been prepared by reactions of the appropriate triarylbismuth compounds and arenesulfonic acids in ether.

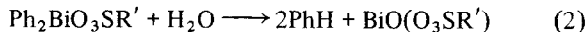


With a large excess of benzenesulfonic or *p*-toluenesulfonic acid at room temperature for a short reaction time, only one aryl group was removed from triphenylbismuth. Tri-*p*-tolylbismuth reacted analogously with an excess of *p*-toluenesulfonic acid and with benzenesulfonic acid on a mole ratio of 1:2. With more aggressive conditions, two Bi–C bonds were cleaved by benzenesulfonic acid and an impure product was obtained which contained $p-MeC_6H_4Bi(O_3SPh)_2$ and presumably (because of a low C, H analysis) $BiO(O_3SPh)$.

The 1H NMR spectra of $R_nBi(O_3SR')_{3-n}$ complexes provide verification of the proposed compositions, since resonances of the different aryl groups (R, R') can be distinguished owing to the downfield shift of *ortho* protons of arylbismuth(III) compounds [7] and the further downfield shift of arylbismuth resonances as aryl groups are replaced by anionic ligands [4, 5]. Although $p-MeC_6H_4Bi(O_3SPh)_2$ was not isolated in a pure form, it was clearly identified by observation of a resonance attributable to *ortho* hydrogens of a *p*-tolylbismuth group downfield from the corresponding resonance of $(p-MeC_6H_4)_2BiO_3SPh$. Where the aryl groups R and R' [see reaction (1)] differ, the presence of both groups can be established by IR spectroscopy. In addition, $\gamma(CH)$ absorptions of the different $p-MeC_6H_4$ groups of $(p-MeC_6H_4)_2BiO_3S-p-MeC_6H_4$ can be observed separately (816 cm^{-1} for $p-MeC_6H_4S$; 796 cm^{-1} for $p-MeC_6H_4Bi$). In the case of Ph_2BiO_3SPh , for which an assignment of the IR absorption ($1300\text{--}500$

cm^{-1}) is given in the Experimental Section, the $\gamma(\text{CH})$ absorption f of the PhS group gives medium absorption at 760 cm^{-1} , but there is coincidence between the 'X-sensitive mode', r , of the PhSO_3 group and the $\gamma(\text{CH})$ mode, f , of the Ph_2Bi group. (For relevant assigned spectra, see refs. 5, 8–10.) The arylbismuth(III) sulfonates show intense absorption attributable [9, 10] to sulfur–oxygen stretching of coordinated arenesulfonate ligands at *ca.* 1260, 1070, and 990 cm^{-1} (see Experimental). However, the exact nature (unidentate, bridging, chelating) of the sulfonate bonding cannot be established by vibrational spectroscopy [8–10]. Organobismuth(III) carboxylates have bidentate or bridging bidentate carboxylate groups [5], and an analogous situation is likely here to provide bismuth with a reasonable coordination number of four or five.

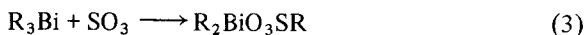
On prolonged storage, $\text{Ph}_2\text{BiO}_3\text{SR}'$ ($\text{R}' = \text{Ph}$ or $p\text{-MeC}_6\text{H}_4$) loses the phenyl groups from bismuth. The ^1H NMR spectra of the products show only the aryl groups attached to sulfur, and the analytical composition of the products corresponds approximately to $\text{BiO}(\text{O}_3\text{SR}')$. The $\nu(\text{S}-\text{O})$ absorptions at *ca.* $1250\text{--}1100\text{ cm}^{-1}$ are considerably broadened from those of the $\text{Ph}_2\text{BiO}_3\text{SR}'$ parent compounds. A broad absorption attributable to $\nu(\text{Bi}-\text{O})$ [11, 12] was evident at $570\text{--}550\text{ cm}^{-1}$. Presumably, slow hydrolysis by atmospheric moisture occurs.



Arylbismuth(III) acetates and trifluoroacetates readily hydrolyse to the corresponding arenes on exposure to air [5]. In addition to hydrolysis, some rearrangement of $\text{Ph}_2\text{BiO}_3\text{SR}'$ occurs on standing, since a small amount of triphenylbismuth was detected in the products and may account for somewhat high percentage C, H found for $\text{BiO}(\text{O}_3\text{SPh})$.

(b) Reactions with Sulfur Trioxide

Treatment of triphenylbismuth with sulfur trioxide according to the reported procedure [1] gave a product with IR and ^1H NMR spectra identical to those of diphenylbismuth(III) benzenesulfonate. The IR spectrum was also in agreement with that reported for $\text{Ph}_3\text{Bi}\cdot\text{SO}_3$ [1], the spectrum of which clearly shows absorption now attributable to $\gamma(\text{CH})$ f of PhSO_3 . Thus, the occurrence of sulfur trioxide insertion is indicated [reaction (eqn. 3), $\text{R} = \text{Ph}$]. The

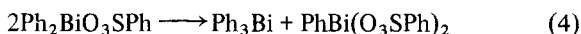


yield of $\text{Ph}_2\text{BiO}_3\text{SPh}$ (*ca.* 50%) was higher than in the earlier preparation which gave *ca.* 25% of ' $\text{Ph}_3\text{Bi}\cdot\text{SO}_3$ ' [1]. The reaction also gave an insoluble residue, which was identified by analysis and IR spectroscopy as a mixture of basic bismuth(III) sulfate and basic bismuth(III) benzenesulfonate. This is in contrast

to the previous report [1], in which a 60% yield of basic bismuth sulfate was found. Thus, it would appear that water was more effectively excluded in the present study.

A similar reaction with tri-*p*-tolylbismuth gave $(p\text{-MeC}_6\text{H}_4)_2\text{BiO}_3\text{S-}p\text{-MeC}_6\text{H}_4$ as a major product (reaction (3), $\text{R} = p\text{-MeC}_6\text{H}_4$), but the ^1H NMR spectrum also showed an *ortho* proton resonance of a $p\text{-MeC}_6\text{H}_4\text{Bi}$ group downfield from that of the bis(*p*-tolyl)bismuth compound; this can be confidently attributed to $p\text{-MeC}_6\text{H}_4\text{Bi}(\text{O}_3\text{S-}p\text{-MeC}_6\text{H}_4)_2$. Thus tri-*p*-tolylbismuth is cleaved more extensively than triphenylbismuth by sulfur trioxide.

There remains to explain the reported formation [1] of triphenylbismuth on treatment of ' $\text{Ph}_3\text{Bi}\cdot\text{SO}_3$ ' with boiling water. Repeating the reaction with $\text{Ph}_2\text{BiO}_3\text{SPh}$ from both reactions (1) and (3) confirmed this behaviour (see Experimental). However, inorganic bismuth and benzenesulfonate ions were also obtained but no sulfate ions, contrary to the initial report. The formation of triphenylbismuth can be attributed to the rearrangement (eqn. 4). Di-*p*-tolylbismuth(III) trifluoroacetate



undergoes a similar reaction in $(\text{CD}_3)_2\text{SO}$ at room temperature [5]. Formation of inorganic bismuth presumably derives from hydrolysis of $\text{PhBi}(\text{O}_3\text{SPh})_2$, for which there is a precedent (see [5] and reaction (eqn. 2)). It is remarkable that eqn. 4 appears to be sufficiently fast to precede hydrolysis, considering the fact that $\text{Ph}_2\text{BiO}_3\text{SR}'$ ($\text{R}' = \text{Ph}$ or $p\text{-MeC}_6\text{H}_4$) compounds yield $\text{BiO}(\text{O}_3\text{SR}')$ and only very small amounts of triphenylbismuth on prolonged storage.

Experimental

Reagents

Triphenylbismuth, benzenesulfonic acid and *p*-toluenesulfonic acid were used as supplied by E. Merck, Darmstadt. Tri-*p*-tolylbismuth was prepared by reaction of bismuth trichloride with the appropriate Grignard reagent obtained from $p\text{-MeC}_6\text{H}_4\text{-Br}$ [13]. Dry gaseous sulfur trioxide was prepared by bubbling a stream of dry nitrogen through oleum (65%). Solvents were purified and dried before use according to literature methods. All reactions were carried out under dry nitrogen.

Analysis

C and H were determined microanalytically as usual [6].

Instrumentation

IR spectra of Nujol mulls were recorded with a Perkin-Elmer PE 580B spectrophotometer and KBr

was used as window material. ¹H NMR spectra were measured at 90 MHz on a Perkin-Elmer R 32 spectrometer, with CD₃OD as solvent. Chemical shifts are in ppm downfield from internal Me₄Si. Integrations were as expected for the proposed compositions. In assignments, aryl groups attached to bismuth are designated R and those attached to sulfur are designated R'.

Syntheses

Ph₂BiO₃SPh

A solution of triphenylbismuth (0.46 g, 1.05 mmol) in diethyl ether (15 ml) and a solution of benzenesulfonic acid (5.0 g, 28.4 mmol) in diethyl ether (25 ml) were mixed and stirred at room temperature for 15 min. The precipitate which formed was collected, washed with diethyl ether and dried at room temperature to give the required product (0.46 g, 0.89 mmol, 84%); melting point 250 °C (decomposition). *Anal.* Found: C, 41.8; H, 3.0. Calc. for BiC₁₈H₁₅O₃S: C, 41.5; H, 2.9%. IR absorption: 1252s [ν(SO₃)], 1190w [α, β(CH), a₁, R, R'], 1165w [c, β(CH), b₂, R, R'], 1122m and 1112m [q, 'X-sens', a₁, R'], 1072s [ν(SO₃)], 1030w [b, β(CH), a₁; R, R'], 1008m [p, ring, a₁, R'], 990s [ν(SO₃) + p, ring a₁, R], 760m [f, γ(CH), b₁, R'], 730s [f, γ(CH), b₁, R + r, 'X-sens', a₁, R'], 693m [ν, φ(CC), b₁, R, R'], 610s [SO₃ def.], 562m [SO₃ def.], 470w [y, 'X-sens', b₁, R, R'], 440w [t, 'X-sens', a₁, R] cm⁻¹. ¹H NMR (CD₃OD): 8.09, d (o-H, R); 7.77, m (m-H, R; o-H, R'); 7.36, m (p-H, R; m- and p-H, R').

Ph₂BiO₃S-p-MeC₆H₄

Similarly the reaction of triphenylbismuth (0.46 g, 1.05 mmol) and p-toluenesulfonic acid (5.0 g, 26.3 mmol) in diethyl ether (40 ml) gave the required product (0.45 g, 0.84 mmol, 79%); melting point 196 °C (decomposition). *Anal.* Found: C, 42.7; H, 3.3. Calc. for BiC₁₉H₁₇O₃S: C, 42.7; H, 3.2%. IR absorption: 1248s, 1190w, 1158w, 1125s, 1111s, 1075s, 1024m, 1015w, 995s, 815m, 728s, 695m, 683s, 570m cm⁻¹. ¹H NMR (CD₃OD): 8.29, d (o-H, R); 7.74, t (m-H, R); 7.42, m (p-H, R; o-H, R'); 7.10, d (m-H, R'); 2.27, s (Me).

(p-MeC₆H₄)₂BiO₃S-p-MeC₆H₄

The reaction of tri-p-tolylbismuth (0.73 g, 1.51 mmol) and p-toluenesulfonic acid (5.0 g, 26.3 mmol) was performed analogously and gave the required product (0.68 g, 1.21 mmol, 80%); melting point 199 °C (decomposition). *Anal.* Found: C, 45.1; H, 3.8. Calc. for BiC₂₁H₂₁O₃S: C, 44.8; H, 3.8%. IR absorption: 1255s, 1210w, 1190w, 1115m, 1072s, 1028m, 1015w, 998s, 816m, 796s, 725w, 680m, 575w, 565m, 555m, 480m cm⁻¹. ¹H NMR (CD₃OD): 8.23 d (o-H, R); 7.64, m (m-H, R; o-H, R'); 7.19, d (m-H, R'); 2.36 s (Me).

Reaction of (p-MeC₆H₄)₃Bi with PhSO₃H

(a) A solution of tri-p-tolylbismuth (0.73 g, 1.51 mmol) and benzenesulfonic acid (0.60 g, 3.41 mmol) in diethyl ether (40 ml) was stirred for 2 h. The precipitate which formed was collected, washed with diethyl ether and dried at room temperature to give (p-MeC₆H₄)₂BiO₃SPh (0.81 g, 1.48 mmol, 98%); melting point >250 °C (decomposition). *Anal.* Found: C, 43.6; H, 3.4; Calc. for BiC₂₀H₁₉O₃S: C, 43.8; H, 3.5%. IR absorption: 1248s, 1235w, 1188w, 1122s, 1075s, 1060w, 1055w, 1030w, 1008m, 998s, 795m, 763m, 730m, 692w 610s, 570w, 565m, 475m cm⁻¹. ¹H NMR (CD₃OD): 8.18, d (o-H, R); 7.60, m (m-H, R; o-H, R'); 7.33 m (m- and p-H, R'); 2.33, s (Me).

(b) Tri-p-tolylbismuth (0.73 g, 1.51 mmol) and benzenesulfonic acid (0.60 g, 3.41 mmol) were refluxed in diethyl ether (40 ml) for 17 h. The resulting precipitate of impure p-MeC₆H₄Bi(O₃SPh)₂ was collected and washed with diethyl ether (0.85 g, 1.38 mmol, 92%); melting point 228 °C (decomposition). *Anal.* Found: C, 33.4; H, 3.0. Calc. for BiC₁₉H₁₇O₆S₂: C, 37.1, H, 3.1%, and possibly contained some BiO(O₃SPh). IR absorption: 1270s, 1247w, 1195w, 1160w, 1125s, 1105m, 1080s, 1065vs, 1035s, 1018m, 1010s, 990s, 797m, 763m, 757m, 727m, 690m, 615m, 607s, 575w, 565w, 545w, 480w cm⁻¹. ¹H NMR (CD₃OD): 8.66, d (o-H, R); 7.81, m (m-H, R; o-H, R'); 7.37, m (m- and p-H, R'). 2.31, s (Me).

Reaction of Ph₃Bi with SO₃

Dry gaseous sulfur trioxide was bubbled through a solution of triphenylbismuth (10 g, 22.7 mmol) in 1,2-dichloroethane (40 ml) for 2 h at -10 °C. On addition of diethyl ether (400 ml), a white precipitate was formed. This was filtered off and extracted 3 times with dry ethanol (3 × 50 ml). The insoluble residue (0.90 g) contained some BiO(O₃SPh). *Anal.* Found: C, 10.5; H, 1.1. Calc. for BiC₆H₅O₄S: C, 18.9; H, 1.3%. On addition of petroleum ether (boiling point ~40 °C) to the ethanol extracts, a white solid was precipitated, filtered off, washed with diethyl ether and dried (3.2 g, 6.5 mmol, 27%); melting point 244 °C (decomposition) literature [1] melting point of 'Ph₃Bi·SO₃', 236 °C. *Anal.* Found: C, 41.8; H, 3.0. Calc. for BiC₁₈H₁₅O₃S: C, 41.5; H, 2.9%. The IR and ¹H NMR spectra were identical with those of authentic Ph₂BiO₃SPh. Further pure product (3.0 g, 25%) was obtained on evaporation of the filtrate to dryness.

Reaction of (p-MeC₆H₄)₃Bi with SO₃

Dry gaseous sulfur trioxide was bubbled through a solution of tri-p-tolylbismuth (6.0 g, 12.4 mmol) in 1,2-dichloroethane (30 ml) for 2 h at -10 °C. On addition of diethyl ether (300 ml), a white precipitate was formed. This was filtered off and extracted

with ethanol as above. The insoluble residue (0.43 g, 1.08 mmol, 8.8%) was analysed as impure $\text{BiO}(\text{O}_3\text{-}p\text{-MeC}_6\text{H}_4)$. *Anal.* Found: C, 17.1; H, 1.8. Calc. for $\text{BiC}_7\text{H}_7\text{O}_4\text{S}$: C, 21.2; H, 1.8%. The filtrate was evaporated to dryness. The residue (2.34 g); melting point 198 °C (decomposition). *Anal.* Found: C, 37.9, H, 3.3%; IR absorption: 1280s, 1250m, 1220w, 1190w, 1125s, 1072s, 1030m, 998s, 815m, 795m, 725w, 680s, 565s, 480m cm^{-1} , contained ($p\text{-MeC}_6\text{H}_4$)₂ $\text{BiO}_3\text{S-}p\text{-MeC}_6\text{H}_4$ (major product), ^1H NMR (CD_3OD): 8.12, d (*o*-H, R); 7.61, d (*o*-H, R'); 7.42 d (*m*-H, R); 7.17 d (*m*-H, R'), 2.33, s (Me), and $p\text{-MeC}_6\text{H}_4\text{Bi}(\text{O}_3\text{S-}p\text{-MeC}_6\text{H}_4)_2$ (minor product), ^1H NMR (CD_3OD): 8.67, d (*o*-H, R); 7.83, d (*m*-H, R); 7.61, d (*o*-H, R'); 7.17, d (*m*-H, R'), 2.33, s (Me).

Behaviour of $\text{Ph}_2\text{BiO}_3\text{SR}'$ ($\text{R}' = \text{Ph}$ or $p\text{-MeC}_6\text{H}_4$) on Standing

Analytical and spectroscopic data for aged (>10 years) samples

Aged $\text{Ph}_2\text{BiO}_3\text{SPh}$. *Anal.* Found C, 20.0; H, 1.6, Calc. for $\text{BiC}_6\text{H}_5\text{O}_4\text{S}$. C, 18.9; H, 1.3%. IR absorption 1245m (br), 1200m (br), 1160s, 1120s, 1075w, 1045m, 1018m, 998m, 755m, 730m, 690m, 610m, 560m (br) [$\nu(\text{BiO})$], 480 w cm^{-1} . ^1H NMR [$(\text{CD}_3)_2\text{SO}$]: 7.63, m (*o*-H), 7.30, m (*m*-, *p*-H) Aged $\text{Ph}_2\text{BiO}_3\text{S-}p\text{-MeC}_6\text{H}_4$. *Anal.* Found C, 21.5; H, 2.0. Calc. for $\text{BiC}_7\text{H}_7\text{O}_4\text{S}$: C, 21.2, H, 1.8%. IR absorption. 1245m (br), 1200s (br), 1160s (br), 1125s (br), 1035s, 1010s, 818m, 725m, 710w, 688s, 570s (br) [$\nu(\text{BiO})$] cm^{-1} ^1H NMR [$(\text{CD}_3)_2\text{SO}$]: 7.59, d (*o*-H); 7.09, d (*m*-H); 2.30, s (Me).

When suspensions of the aged compounds were placed on silica gel plates (Macherey-Nagel, Duren, Alugram SIL G/UV₂₅₄, 0.25 mm), elution with ethanol (96%) gave triphenylbismuth (identified by comparison with an authentic sample).

Decomposition of $\text{Ph}_2\text{BiO}_3\text{SPh}$ in Water

$\text{Ph}_2\text{BiO}_3\text{SPh}$ (0.50 g) was boiled in water (200 ml) for 2 h, and the slightly turbid reaction solution

was extracted with diethyl ether. Triphenylbismuth was identified in the extract by TLC. The extracted solution was filtered (the residue contained Bi(III)), neutralized with NaOH solution, and evaporated to dryness. In the residue, NaO_3SPh was detected by IR spectroscopy (comparison with an authentic spectrum).

Acknowledgements

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