*Inorganica Chimica Acta*, *113* (1986) 43–46

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

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Received June 25, 1985

## 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 triorganobismuthines 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.

## 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.

$$R_3Bi + R'SO_3H \longrightarrow R_2BiO_3SR' + RH \qquad (1)$$

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 (1300–500

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0020-1693/86/$3.50

cm$^{-1}$) is given in the Experimental Section, the $\gamma$(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 $\gamma$(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, $Ph_2BiO_3SR'$ (R' = Ph or $p$-$MeC_6H_4$) loses the phenyl groups from bismuth. The $^1$H NMR spectra of the products show only the aryl groups attached to sulfur, and the analytical composition of the products corresponds approximately to $BiO(O_3SR')$. The $\nu$(S–O) absorptions at *ca.* 1250–1100 cm$^{-1}$ are considerably broadened from those of the $Ph_2BiO_3SR'$ parent compounds. A broad absorption attributable to $\nu$(Bi–O) [11, 12] was evident at 570–550 cm$^{-1}$. Presumably, slow hydrolysis by atmospheric moisture occurs.

$$Ph_2BiO_3SR' + H_2O \longrightarrow 2PhH + BiO(O_3SR') \qquad (2)$$

Arylbismuth(III) acetates and trifluoroacetates readily hydrolyse to the corresponding arenes on exposure to air [5]. In addition to hydrolysis, some rearrangement of $Ph_2BiO_3SR'$ 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 $BiO(O_3SPh)$.

### *(b) Reactions with Sulfur Trioxide*

Treatment of triphenylbismuth with sulfur trioxide according to the reported procedure [1] gave a product with IR and $^1$H NMR spectra identical to those of diphenylbismuth(III) benzenesulfonate. The IR spectrum was also in agreement with that reported for $Ph_3Bi{\cdot}SO_3$ [1], the spectrum of which clearly shows absorption now attributable to $\gamma$(CH) $f$ of $PhSO_3$. Thus, the occurrence of sulfur trioxide insertion is indicated [reaction (eqn. 3), R = Ph]. The

$$R_3Bi + SO_3 \longrightarrow R_2BiO_3SR \qquad (3)$$

yield of $Ph_2BiO_3SPh$ (*ca.* 50%) was higher than in the earlier preparation which gave *ca.* 25% of '$Ph_3Bi{\cdot}SO_3$' [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 $(p\text{-}MeC_6H_4)_2BiO_3S\text{-}p\text{-}MeC_6H_4$ as a major product (reaction (3), R = $p$-$MeC_6H_4$), but the $^1$H NMR spectrum also showed an *ortho* proton resonance of a $p$-$MeC_6H_4Bi$ group downfield from that of the bis($p$-tolyl)bismuth compound; this can be confidently attributed to $p\text{-}MeC_6H_4Bi(O_3S\text{-}p\text{-}MeC_6H_4)_2$. 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 '$Ph_3Bi{\cdot}SO_3$' with boiling water. Repeating the reaction with $Ph_2BiO_3SPh$ 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

$$2Ph_2BiO_3SPh \longrightarrow Ph_3Bi + PhBi(O_3SPh)_2 \qquad (4)$$

undergoes a similar reaction in $(CD_3)_2SO$ at room temperature [5]. Formation of inorganic bismuth presumably derives from hydrolysis of $PhBi(O_3SPh)_2$, 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 $Ph_2BiO_3SR'$ (R' = Ph or $p$-$MeC_6H_4$) compounds yield $BiO(O_3SR')$ 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 $p$-$MeC_6H_4$-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. $^1$H NMR spectra were measured at 90 MHz on a Perkin-Elmer R 32 spectrometer, with $CD_3OD$ as solvent. Chemical shifts are in ppm downfield from internal $Me_4Si$. 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*

### $Ph_2BiO_3SPh$

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 $BiC_{18}H_{15}O_3S$: C, 41.5; H, 2.9%. IR absorption: 1252s [$\nu(SO_3)$], 1190w [*a*, $\beta$(CH), $a_1$, R,R′], 1165w [*c*, $\beta$(CH), $b_2$, R,R′], 1122m and 1112m [*q*, 'X-sens', $a_1$, R′], 1072s [$\nu(SO_3)$], 1030w [b, $\beta$(CH), $a_1$; R,R′], 1008m [*p*, ring, $a_1$, R′], 990s [$\nu(SO_3) + p$, ring $a_1$, R], 760m [*f*, $\gamma$(CH), $b_1$, R′], 730s [*f*, $\gamma$(CH), $b_1$, R + *r*, 'X-sens', $a_1$, R′], 693m [*v*, $\phi$(CC), $b_1$, R,R′], 610s [$SO_3$ def.], 562m [$SO_3$ def.], 470w [y, 'X-sens', $b_1$, R,R′?], 440w [*t*, 'X-sens', $a_1$, R′] cm$^{-1}$. $^1$H NMR ($CD_3OD$): 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′).

### $Ph_2BiO_3S\text{-}p\text{-}MeC_6H_4$

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 $BiC_{19}H_{17}O_3S$: C, 42.7; H, 3.2%. IR absorption: 1248s, 1190w, 1158w, 1125s, 1111s, 1075s, 1024m, 1015w, 995s, 815m, 728s, 695m, 683s, 570m cm$^{-1}$. $^1$H NMR ($CD_3OD$): 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).

### $(p\text{-}MeC_6H_4)_2BiO_3S\text{-}p\text{-}MeC_6H_4$

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 $BiC_{21}H_{21}O_3S$: 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$^{-1}$. $^1$H NMR ($CD_3OD$): 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 $(p\text{-}MeC_6H_4)_3Bi$ with $PhSO_3H$

(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 $(p\text{-}MeC_6H_4)_2BiO_3SPh$ (0.81 g, 1.48 mmol, 98%); melting point >250 °C (decomposition). *Anal.* Found: C, 43.6; H, 3.4; Calc. for $BiC_{20}H_{19}O_3S$: 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$^{-1}$. $^1$H NMR ($CD_3OD$): 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 $p\text{-}MeC_6H_4Bi(O_3SPh)_2$ 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 $BiC_{19}H_{17}O_6S_2$: C, 37.1, H, 3.1%, and possibly contained some $BiO(O_3SPh)$. 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$^{-1}$. $^1$H NMR ($CD_3OD$): 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 $Ph_3Bi$ with $SO_3$

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 $BiO(O_3SPh)$. *Anal.* Found: C, 10.5; H, 1.1. Calc. for $BiC_6H_5O_4S$: 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 '$Ph_3Bi\cdot SO_3$', 236 °C. *Anal.* Found: C, 41.8; H, 3.0. Calc. for $BiC_{18}H_{15}O_3S$: C, 41.5; H, 2.9%. The IR and $^1$H NMR spectra were identical with those of authentic $Ph_2BiO_3SPh$. Further pure product (3.0 g, 25%) was obtained on evaporation of the filtrate to dryness.

### Reaction of $(p\text{-}MeC_6H_4)_3Bi$ with $SO_3$

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 $BiO(O_3S\text{-}p\text{-}MeC_6H_4)$. *Anal.* Found· C, 17.1; H, 1.8 Calc. for $BiC_7H_7O_4S$: 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 $(p\text{-}MeC_6H_4)_2BiO_3S\text{-}p\text{-}MeC_6H_4$ (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 $p\text{-}MeC_6H_4Bi(O_3S\text{-}p\text{-}MeC_6H_4)_2$ (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 $Ph_2BiO_3SR'$ ($R'$ = Ph or $p\text{-}MeC_6H_4$) on Standing*

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

Aged $Ph_2BiO_3SPh$. *Anal.* Found C, 20.0; H, 1.6, Calc. for $BiC_6H_5O_4S$. C, 18.9; H, 1.3%. IR absorption 1245m (br), 1200m (br), 1160s, 1120s, 1075w, 1045m, 1018m, 998m, 755m, 730m, 690m, 610m, 560m (br) [$\nu$(BiO)], 480 w $cm^{-1}$. $^1H$ NMR $[(CD_3)_2SO]$ · 7 63, m (*o*-H), 7.30, m (*m*-, *p*-H) Aged $Ph_2BiO_3S\text{-}p\text{-}MeC_6H_4$ *Anal.* Found C, 21.5; H, 2.0 Calc. for $BiC_7H_7O_4S$: C, 21.2, H, 1.8%. IR absorption. 1245m (br), 1200s (br), 1160s (br), 1125s (br), 1035s, 1010s, 818m, 725m, 710w, 688s, 570s (br) [$\nu$(BiO)] $cm^{-1}$ $^1H$ NMR $[(CD_3)_2SO]$ 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 $G/UV_{254}$, 0.25 mm), elution with ethanol (96%) gave triphenylbismuth (identified by comparison with an authentic sample).

### *Decomposition of $Ph_2BiO_3SPh$ in Water*

$Ph_2BiO_3SPh$ (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

One of us (G.B.D.) is grateful to Monash University for an Outside Studies Programme Grant and to Warman International for support of organobismuth research. We thank Dr. K. Brändle, Farbenfabriken Bayer, Leverkusen for providing $SO_3$, and Miss C, Horch for skillful assistance.

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