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Synthesis and properties of *N*-perfluoroalkylsulfonyltriarylbismuth imines, $Ar_3Bi{=}NSO_2R_f$

Sergei V. Pasenok, Natali V. Kirij and Yurii L. Yagupolskii
Institute of Organic Chemistry, Academy of Sciences of the Ukraine, Murmanskaya 5, 253660 Kiev-94 (Ukraine)

Dieter Naumann* and Wieland Tyrra
Institut für Anorganische Chemie, Universität Köln, Greinstr. 6, D-W5000 Köln 41 (Germany)

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Abstract

Bismuth imines of the general formula $Ar_3Bi{=}NSO_2R_f$ have been prepared either by the reaction of Ar_3BiCl_2 with the corresponding perfluoroalkylsulfonic acid amide in the presence of $NaOCH_3$ or by the reaction of Ar_3BiF_2 with $CF_3SO_2N[Si(CH_3)_3]_2$. Bismuth imines $Ar_3Bi{=}NSO_2R_f$ as well as $(C_6H_5)_3Bi{=}NSO_2$ $(4\text{-}CH_3C_6H_4)$ were obtained as crystalline solids and characterized by NMR spectroscopy, elemental analysis and consecutive reactions.

Introduction

Imines of Main Group V of the Periodic Table with the general formula $R_3E{=}NSO_2R'$ have been described for phosphorus [1], arsenic [2] and antimony [3]. Less is known about the analogous derivatives of bismuth, although Wittig and Hellwinkel [3] in 1964 reported the successful synthesis of $(C_6H_5)_3Bi{=}NSO_2$ $(4\text{-}CH_3C_6H_4)$.

$$(C_6H_5)_3Bi + NaClNSO_2(4\text{-}CH_3C_6H_4) \longrightarrow (C_6H_5)_3Bi{=}NSO_2(4\text{-}CH_3C_6H_4) + NaCl$$

A reinvestigation of this reaction with a refinement of the results was carried out by Suzuki *et al.* [4] who also synthesized arylbismuth imines with substituted aryl groups bound to the bismuth atom as oily or glassy products by the procedure mentioned above.

The only example of a triaryl Main Group V derivative containing an NSO_2R_f group is $(C_6H_5)_3Sb{=}NSO_2CF_3$ which was prepared by Radchenko *et al.* in 1976 [5] according to:

$$(C_6H_5)_3Sb + N_3SO_2CF_3 \longrightarrow (C_6H_5)_3Sb{=}NSO_2CF_3 + N_2$$

We herein report the synthesis of bismuth imines of the general formula $Ar_3Bi{=}NSO_2R$ ($Ar = C_6H_5$, $4\text{-}FC_6H_4$; $R = CF_3$, $n\text{-}C_4F_9$, $4\text{-}CH_3C_6H_4$) by two different, new pathways.

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*To whom all correspondence should be addressed.

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Results and discussion

N-Perfluoroalkyl- and *N*-*p*-tolylsulfonyltriarylbismuth imines are formed by the reaction of triarylbismuth dichlorides with sodium derivatives of sulfonylamides (method A).

$$Ar_3BiCl_2 + H_2NSO_2R + 2CH_3ONa \longrightarrow Ar_3Bi{=}NSO_2R + 2NaCl + 2CH_3OH$$

The reactions proceed in acetonitrile or dichloromethane solution at room temperature within 15 min.

Using this reaction pathway the bismuth imines $Ar_3Bi{=}NSO_2CF_3$ ($Ar = C_6H_5, 4\text{-}FC_6H_4$), $(C_6H_5)_3Bi{=}NSO_2C_4F_9$ and $(C_6H_5)_3Bi{=}NSO_2(4\text{-}CH_3C_6H_4)$ may be obtained as colourless crystalline solids in greater than 90% yield.

All the compounds are readily soluble in dichloromethane, acetonitrile, benzene and several polar solvents. Under dry nitrogen, the solid bismuth imines are stable over a period of more than 1 week; they decompose in solution within 20 h.

Hydrolysis of the bismuth imines finally yields the triarylbismuth oxide in addition to the corresponding sulfonamide. However, in the case of $(4\text{-}FC_6H_4)_3Bi{=}NSO_2CF_3$ intermediates could also be detected in the ^{19}F NMR spectra. Thus, in addition to the 4-F resonance of the starting material, two broad resonances occur at δ −106.79 ppm and δ −107.45 ppm in the ratio 1:2 which may be assigned to $(4\text{-}FC_6H_4)_3Bi(OH)NHSO_2CF_3$ and the condensation product $[(4\text{-}FC_6H_4)_3BiNHSO_2CF_3]_2O$. Hence, the following mechanism of hydrolysis is proposed using Mann's approach to the *N*-*p*-tolylsulfonylarsenic imines [2].

$$(4\text{-}FC_6H_4)_3Bi{=}NSO_2CF_3 + H_2O \rightleftharpoons (4\text{-}FC_6H_4)_3Bi(OH)NHSO_2CF_3$$

$$2(4\text{-}FC_6H_4)_3Bi(OH)NHSO_2CF_3 \longrightarrow [(4\text{-}FC_6H_4)_3BiNHSO_2CF_3]_2O + H_2O$$

$$(4\text{-}FC_6H_4)_3Bi(OH)NHSO_2CF_3 \longrightarrow (4\text{-}FC_6H_4)_3BiO + H_2NSO_2CF_3$$

With an excess of acetic and trifluoroacetic anhydrides, $(C_6H_5)_3Bi{=}NSO_2CF_3$ reacts to form the corresponding triphenylbismuth diacetates which could be identified by their melting points [6, 7].

An alternative route to bismuth imines is the reaction of triarylbismuth difluoride with *N*,*N*-bis(trimethylsilyl)trifluoromethylsulfonylamides (method B) which was studied on the system $(C_6H_5)_3BiF_2/[(CH_3)_3Si]_2NSO_2CF_3$.

From the reaction in benzene at 40 °C, $(C_6H_5)_3Bi{=}NSO_2CF_3$ could be obtained in nearly quantitative yield according to:

$$(C_6H_5)_3BiF_2 + [(CH_3)_3Si]_2NSO_2CF_3 \longrightarrow (C_6H_5)_3Bi{=}NSO_2CF_3 + 2(CH_3)_3SiF$$

Attempts to obtain bismuth imines via a direct route from triarylbismuth and *N*,*N*-dichlorotrifluoromethylsulfonylamides failed. In all cases a product mixture of Ar_3BiCl_2 and $Ar_3Bi{=}NSO_2CF_3$ was obtained from which the imine could not be separated.

All compounds were identified by their ^{19}F and ^{1}H NMR spectra as well as by elemental analyses. ^{13}C NMR spectra could not be obtained because the samples decomposed slowly in the solvents during the time required for obtaining spectra. The mass spectra especially of $(C_6H_5)_3Bi{=}NSO_2CF_3$ showed a low-intensity molecular peak but they were dominated by fragments arising from the decay of triarylbismuth [8].

Experimental

Literature methods were used for the synthesis of $(C_6H_5)_3BiCl_2$ [9], $(4\text{-}FC_6H_4)_3BiCl_2$ by analogy to ref. 9, $(C_6H_5)_3BiF_2$ [6], $CF_3SO_2NH_2$ [10], $n\text{-}C_4F_9SO_2NH_2$ [11] and $CF_3SO_2N[Si(CH_3)_3]_2$ [12]. All solvents were purified by common methods [13]. All compounds were handled in a dry N_2 atmosphere using Schlenk techniques.

The ^{19}F NMR spectra were recorded on a Bruker model WP 200 spectrometer (^{19}F, 188.3 MHz) or on a Bruker model AC 200 spectrometer, the ^1H NMR spectra on a Gemini 200 spectrometer with positive shifts being downfield from the standards external CCl_3F (^{19}F) and internal TMS (^1H).

The mass spectra were recorded on a modified Varian CH 5 mass spectrometer with a source temperature of 180 °C.

Preparation of N-*trifluoromethylsulfonyltriphenylbismuth imine*

Method A

To a sodium methylate solution, obtained from 0.048 g (2.0 mmol) NaH in 2 ml CH_3OH, 0.149 g (1.0 mmol) trifluoromethanesulfonic acid amide was added. The reaction mixture was stirred for 10 min and the CH_3OH then distilled off *in vacuo*. CH_3CN (10 ml) was added to the dry residue and 0.511 g (1 mmol) $(C_6H_5)_3BiCl_2$ added to the resulting suspension. After stirring the reaction mixture for 15 min at ambient temperature, the precipitate (NaCl) was filtered off and washed with 5 ml CH_3CN. Acetonitrile was evaporated and the remaining residue dried *in vacuo*. $(C_6H_5)_3Bi{=}NSO_2CF_3$ was obtained in 95% yield (0.558 g).

Method B

A mixture consisting of 0.478 g (1.0 mmol) $(C_6H_5)_3BiF_2$ and 0.293 g (1.0 mmol) $[(CH_3)_3Si]_2NSO_2CF_3$ in 10 ml C_6H_6 was stirred for approximately 1 h at 40 °C until the evolution of $(CH_3)_3SiF$ had finished. The solvent was distilled off *in vacuo*. $(C_6H_5)_3Bi{=}NSO_2CF_3$ was obtained in nearly quantitative yield.

M.p. 142–144 °C. Elemental analysis for $C_{19}H_{15}BiF_3NO_2S$ [found (calculated)]: C, 39.15% (38.85%); H, 2.71% (2.57%); F, 9.28% (9.70%); N, 2.23% (2.38%); S, 5.10% (5.46%). Cryoscopic molecular weight determination in dioxan, 528 g mol^{-1} (calc., 587 g mol^{-1}). ^{19}F NMR (CD_2Cl_2) δ: -78.26 ppm. ^1H NMR (CD_2Cl_2) δ: 7.43–7.66 (broad multiplets) ppm.

Preparation of N-*trifluoromethylsulfonyltris(4-fluorophenyl)bismuth imine*

The compound was prepared according to method A above from 0.149 g (1.0 mmol) $CF_3SO_2NH_2$ and 0.565 g (1.0 mmol) $(4\text{-}FC_6H_4)_3BiCl_2$ in 93% yield (0.596 g).

M.p. 136 °C (dec.). Elemental analysis for $C_{19}H_{12}BiF_6NO_2S$ [found (calculated)]: C, 35.66% (35.58%); H, 2.09% (1.89%); N, 1.93% (2.18%). ^{19}F NMR (CD_3CN) δ: -79.01 (CF_3); -106.01 (4-F) ppm; (CD_2Cl_2) δ: -78.19 (CF_3); -104.84 (4-F) ppm. ^1H NMR ($CDCl_3$) δ: 7.35 – 7.78 (broad multiplets) ppm.

Preparation of N-nonafluorobutylsulfonyltriphenylbismuth imine

This derivative was prepared according to method A above from 0.299 g (1.00 mmol) n-$C_4F_9SO_2NH_2$ and 0.511 g (1.00 mmol) $(C_6H_5)_3BiCl_2$ in 93% yield (0.686 g).

M.p. 85 °C (dec.). Elemental analysis for $C_{22}H_{15}BiF_9NO_2S$ [found (calculated)]: C, 36.05% (35.83%); H, 2.31% (2.05%); N, 2.18% (1.90%). ^{19}F NMR (CD_3CN) δ: -80.46 (CF_3); -112.68 (α-CF_2); -120.27 (β-CF_2); -125.32 (γ-CF_2) ppm. ^1H NMR (CD_2Cl_2) δ: 7.60 – 8.00 (broad multiplets) ppm.

Preparation of N-tosyltriphenylbismuth imine

The imine was prepared according to method A above from 0.171 g (1.00 mmol) 4-$CH_3C_6H_4SO_2NH_2$ and 0.511 g (1.00 mmol) $(C_6H_5)_3BiCl_2$ in 97% yield (0.591 g).

M.p. 68–70 °C. Elemental analysis for $C_{25}H_{22}BiNO_2S$ [found (calculated)]: C, 49.39% (49.27%); H, 3.88% (3.64%); N, 2.55% (2.30%). ^1H NMR (CD_2Cl_2) δ: 2.37 (s, 3H, CH_3); 7.10–7.70 (m, 19H) ppm. The analytical data corresponded to those given in ref. 4.

Hydrolysis of $(C_6H_5)_3Bi{=}NSO_2CF_3$

Water (1 ml) was added to a solution of 0.587 g (1.00 mmol) $(C_6H_5)_3Bi{=}NSO_2CF_3$ in 10 ml dioxan. The reaction mixture was stirred for 24 h at ambient temperature. During that period a white solid precipitated which was filtered off and identified by its melting point (152–154 °C) as $(C_6H_5)_3BiO$ [14] (0.429 g; 94%). The solvent was evaporated and 0.134 g (90%) $CF_3SO_2NH_2$ with a melting point of 120–122 °C [10] was extracted with n-heptane from the residue.

Reactions of $(C_6H_5)_3Bi{=}NSO_2CF_3$ with $(CH_3CO)_2O$ and $(CF_3CO)_2O$ (by analogy to ref. 3)

Mixtures of 0.587 g (1.00 mmol) $(C_6H_5)_3Bi{=}NSO_2CF_3$ and 5 ml of the corresponding anhydride were stirred for 30 min at 60 °C. The mixture was poured into water. $(C_6H_5)_3Bi(OCOCH_3)_2$ and $(C_6H_5)_3Bi(OCOCF_3)_2$ were filtered off and identified by their melting points $(C_6H_5)_3Bi(OCOCH_3)_2$, m.p. 152 °C [7]; $(C_6H_5)_3Bi(OCOCF_3)_2$, m.p. 133 °C [6].

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