

Synthesis and properties of N-perfluoroalkylsulfonyltriarylbismuth imines, $\text{Ar}_3\text{Bi}=\text{NSO}_2\text{R}_f$

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)

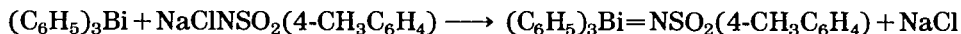
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Abstract

Bismuth imines of the general formula $\text{Ar}_3\text{Bi}=\text{NSO}_2\text{R}_f$ 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 $\text{CF}_3\text{SO}_2\text{N}[\text{Si}(\text{CH}_3)_3]_2$. Bismuth imines $\text{Ar}_3\text{Bi}=\text{NSO}_2\text{R}_f$, as well as $(\text{C}_6\text{H}_5)_3\text{Bi}=\text{NSO}_2(4\text{-CH}_3\text{C}_6\text{H}_4)$ were obtained as crystalline solids and characterized by NMR spectroscopy, elemental analysis and consecutive reactions.

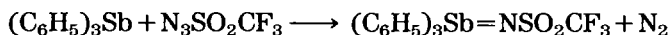
Introduction

Imines of Main Group V of the Periodic Table with the general formula $\text{R}_3\text{E}=\text{NSO}_2\text{R}'$ 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 $(\text{C}_6\text{H}_5)_3\text{Bi}=\text{NSO}_2(4\text{-CH}_3\text{C}_6\text{H}_4)$.



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 $(\text{C}_6\text{H}_5)_3\text{Sb}=\text{NSO}_2\text{CF}_3$ which was prepared by Radchenko *et al.* in 1976 [5] according to:

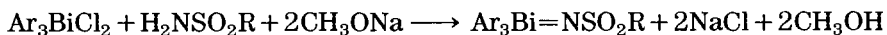


We herein report the synthesis of bismuth imines of the general formula $\text{Ar}_3\text{Bi}=\text{NSO}_2\text{R}$ ($\text{Ar}=\text{C}_6\text{H}_5$, $4\text{-FC}_6\text{H}_4$; $\text{R}=\text{CF}_3$, $n\text{-C}_4\text{F}_9$, $4\text{-CH}_3\text{C}_6\text{H}_4$) by two different, new pathways.

*To whom all correspondence should be addressed.

Results and discussion

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

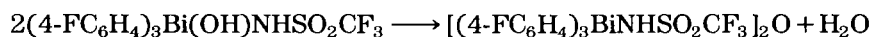
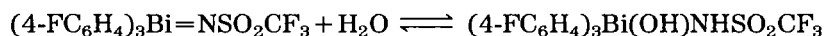


The reactions proceed in acetonitrile or dichloromethane solution at room temperature within 15 min.

Using this reaction pathway the bismuth imines $\text{Ar}_3\text{Bi}=\text{NSO}_2\text{CF}_3$ ($\text{Ar} = \text{C}_6\text{H}_5$, 4- FC_6H_4), $(\text{C}_6\text{H}_5)_3\text{Bi}=\text{NSO}_2\text{C}_4\text{F}_9$ and $(\text{C}_6\text{H}_5)_3\text{Bi}=\text{NSO}_2(4\text{-CH}_3\text{C}_6\text{H}_4)$ 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.

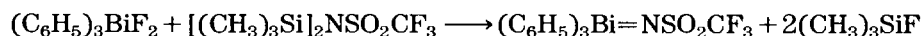
Hydrolysis of the bismuth imines finally yields the triarylbismuth oxide in addition to the corresponding sulfonamide. However, in the case of $(4\text{-FC}_6\text{H}_4)_3\text{Bi}=\text{NSO}_2\text{CF}_3$ intermediates could also be detected in the ^{19}F NMR spectra. Thus, in addition to the 4-F resonance of the starting material, two broad resonances occur at $\delta -106.79$ ppm and $\delta -107.45$ ppm in the ratio 1:2 which may be assigned to $(4\text{-FC}_6\text{H}_4)_3\text{Bi}(\text{OH})\text{NHSO}_2\text{CF}_3$ and the condensation product $[(4\text{-FC}_6\text{H}_4)_3\text{BiNHSO}_2\text{CF}_3]_2\text{O}$. Hence, the following mechanism of hydrolysis is proposed using Mann's approach to the *N-p*-tolylsulfonylarsenic imines [2].



With an excess of acetic and trifluoroacetic anhydrides, $(\text{C}_6\text{H}_5)_3\text{Bi}=\text{NSO}_2\text{CF}_3$ 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 $(\text{C}_6\text{H}_5)_3\text{BiF}_2/[(\text{CH}_3)_3\text{Si}]_2\text{NSO}_2\text{CF}_3$.

From the reaction in benzene at 40 °C, $(\text{C}_6\text{H}_5)_3\text{Bi}=\text{NSO}_2\text{CF}_3$ could be obtained in nearly quantitative yield according to:



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 $\text{Ar}_3\text{Bi}=\text{NSO}_2\text{CF}_3$ was obtained from which the imine could not be separated.

All compounds were identified by their ^{19}F and ^1H 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 $(\text{C}_6\text{H}_5)_3\text{Bi}=\text{NSO}_2\text{CF}_3$ showed a low-intensity molecular peak but they were dominated by fragments arising from the decay of triaryl bismuth [8].

Experimental

Literature methods were used for the synthesis of $(\text{C}_6\text{H}_5)_3\text{BiCl}_2$ [9], $(4\text{-FC}_6\text{H}_4)_3\text{BiCl}_2$ by analogy to ref. 9, $(\text{C}_6\text{H}_5)_3\text{BiF}_2$ [6], $\text{CF}_3\text{SO}_2\text{NH}_2$ [10], $n\text{-C}_4\text{F}_9\text{SO}_2\text{NH}_2$ [11] and $\text{CF}_3\text{SO}_2\text{N}[\text{Si}(\text{CH}_3)_3]_2$ [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) $(\text{C}_6\text{H}_5)_3\text{BiCl}_2$ 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*. $(\text{C}_6\text{H}_5)_3\text{Bi}=\text{NSO}_2\text{CF}_3$ was obtained in 95% yield (0.558 g).

Method B

A mixture consisting of 0.478 g (1.0 mmol) $(\text{C}_6\text{H}_5)_3\text{BiF}_2$ and 0.293 g (1.0 mmol) $[(\text{CH}_3)_3\text{Si}]_2\text{NSO}_2\text{CF}_3$ in 10 ml C_6H_6 was stirred for approximately 1 h at 40 °C until the evolution of $(\text{CH}_3)_3\text{SiF}$ had finished. The solvent was distilled off *in vacuo*. $(\text{C}_6\text{H}_5)_3\text{Bi}=\text{NSO}_2\text{CF}_3$ was obtained in nearly quantitative yield.

M.p. 142–144 °C. Elemental analysis for $\text{C}_{19}\text{H}_{15}\text{BiF}_3\text{NO}_2\text{S}$ [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) $\text{CF}_3\text{SO}_2\text{NH}_2$ and 0.565 g (1.0 mmol) $(4\text{-FC}_6\text{H}_4)_3\text{BiCl}_2$ 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 ($\alpha-CF_2$); -120.27 ($\beta-CF_2$); -125.32 ($\gamma-CF_2$) 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].

Acknowledgement

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