Journal of Fluorine Chemistry, *66* (1994) 75–78

Synthesis of bismuthio methanides containing the R_fSO_2 group, $(C_6H_5)_3Bi{=}C(SO_2R_f)_2$ [$R_f{=}CF_3$, n-C_4F_9, $OCH_2CF_2CF_2H$]

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(Received December 2, 1992; accepted February 22, 1993)

Abstract

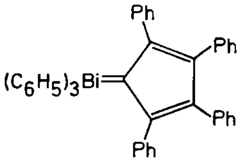
Bismuthio methanides $(C_6H_5)_3Bi{=}C(SO_2R_f)_2$ ($R_f{=}CF_3$, n-C_4F_9, $OCH_2CF_2CF_2H$) can be obtained as colourless solids from the sodium derivatives of the corresponding methanes with $(C_6H_5)_3BiCl_2$ in *c.* 90% yield. The compounds have been characterized by NMR spectroscopy and elemental analysis. From the NMR spectra, zwitterionic canonical structures containing $Bi^+{-}C^-$ or $Bi^+{-}C{=}S{-}O^-$ units may be assumed.

Introduction

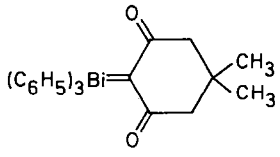
Bismuthio methanides are the least understood carbon–heteroatom ylides. The first example of a bismuthio ylide was prepared by Lloyd and Singer in 1967 [1]. They obtained 2,3,4,5-tetraphenyl-1-triphenylbismuthiocyclopenta-2,4-dienide (A) as a deep blue product contaminated with a small amount of triphenylbismuth from the carbenic decomposition of diazotetraphenylcyclopentadiene in a triphenylbismuth melt. This derivative was the subject of a comparative study of similar compounds of Main Groups 5 and 6 [2].

In 1985, Barton *et al.* [3] described a new type of bismuthio ylide as a product of the reaction of $(C_6H_5)_3BiCO_3$ with dimedone (5,5-dimethylcyclohexane-1,3-dione) under acidic conditions. 4,4-Dimethyl-2,6-dioxo-1-triphenylbismuthiocyclohexanide (B) was obtained as a gum and characterized by ^1H NMR and UV spectroscopy, mass spectrometry and elemental analysis.

A series of compounds derived from 1,3-diones were prepared and their properties intensively studied by Suzuki and co-workers [4–7] who obtained these derivatives either by the method described by Barton *et al.* [3] or from the reaction of $(C_6H_5)_3BiCl_2$ with the sodium derivatives of the corresponding 1,3-diones. In 1990, Suzuki and co-workers showed via an X-ray structural determination of 4,4-dimethyl-2,6-dioxo-1-triphenylbismuthiocyclohexanide (B) that the Bi–C(methanide) bond is not significantly shorter than the Bi–(C-1) bonds of the phenyl substituents and they postulated that the Bi–C(methanide) bond is polarized as $Bi^+{-}C^-$ or $Bi^+{-}C{=}C{-}O^-$ [8].



A



B

$(C_6H_5)_3Bi{=}C(SO_2C_6H_5)_2$ **C**

$(C_6H_5)_3Bi{=}C(SO_2R_f)_2$ **D**

a: $R_f = CF_3$
b: $R_f = n\text{-}C_4F_9$
c: $R_f = OCH_2CF_2CF_2H$

Triphenylbismuthio bis(phenylsulfonyl)methanide (C) has been prepared from triphenylbismuth and diazobis(phenylsulfonyl)methane in benzene or toluene using copper(II) hexafluoropentanedionate as a catalyst [9, 10].

Less is known about methanides containing R_fSO_2 groups (D). So far the only examples described have

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SSDI 0022-1139(93)02898-O

been derivatives of iodine [11, 12], sulfur and pyridine [12].

In continuation of our investigations on perfluoroalkylsulfonyl imines [13] and fluorosulfonyl methanides [14], we describe here the synthesis of triphenylbismuthio bis(polyfluoro-organosulfonyl)methanides as derivatives containing a strong electron-withdrawing R_fSO_2 substituent.

Results and discussion

Triphenylbismuthio bis(polyfluoro-organosulfonyl)methanides can be prepared in a similar manner to the corresponding *N*-perfluoroalkylsulfonyl imines [13] from the reaction of $(C_6H_5)_3BiCl_2$ with the sodium derivatives of bis(polyfluoro-organosulfonyl)methanides.

$$(C_6H_5)_3BiCl_2 + H_2C(SO_2R_f)_2 + 2NaOCH_3 \longrightarrow$$
$$(C_6H_5)_3Bi{=}C(SO_2R_f)_2 + 2NaCl + 2CH_3OH \quad (1)$$

$(R_f{=}CF_3,\ C_4F_9,\ OCH_2CF_2CF_2H)$

The reactions proceed in acetonitrile solution within 30 min. After evaporation of the solvent the bismuthio methanides $(C_6H_5)_3Bi{=}C(SO_2R_f)_2$ can be obtained as colourless solids in 86–95% yield.

Attempts to obtain the trifluoromethyl derivative from the reaction of $(C_6H_5)_3BiCO_3$ with bis(trifluoromethylsulfonyl)methane failed.

Signals of the bismuthio methanide were detected in the NMR spectra of the reaction mixtures. However, after 10 min resonances corresponding to $H_2C(SO_2CF_3)_2$ could again be detected in the spectra of the solution. All attempts to isolate the bismuthio methanide failed. Taken together with the observed evolution of CO_2 and precipitation of $(C_6H_5)_3BiO$, these NMR spectroscopic results imply the following reaction sequence:

$$(C_6H_5)_3BiCO_3 + H_2C(SO_2CF_3)_2 \longrightarrow$$
$$(C_6H_5)_3Bi{=}C(SO_2CF_3)_2 + H_2O + CO_2 \quad (2)$$

$$(C_6H_5)_3Bi{=}C(SO_2CF_3)_2 + H_2O \longrightarrow$$
$$(C_6H_5)_3BiO + H_2C(SO_2CF_3)_2 \quad (3)$$

As solids, the bismuthio methanides are stable for several days. All the compounds were soluble in dichloromethane and acetonitrile, but decomposed in these solvents within a few hours with precipitation of a white solid. Thus, $(C_6H_5)_3Bi{=}C(SO_2CF_3)_2$ decomposed in acetonitrile to give a mixture of six compounds containing CF_3SO_2 groups as determined from the ^{19}F NMR spectra. All resonances are located in the region between δ −74.5 ppm and δ −84.9 ppm. From comparative studies, three of the resonances may be assigned to the signals of $H_2C(SO_2CF_3)_2$ and the anions $[C(SO_2CF_3)_2]^{2-}$ and $[HC(SO_2CF_3)_2]^-$, respectively. In the ^1H NMR spectrum of the solution, an intense singlet of benzene at δ 7.36 ppm, as well as broad resonances corresponding to $H_2C(SO_2CF_3)_2$ and $[HC(SO_2CF_3)_2]^-$, may be detected together with a couple of low intensity signals located in the region between δ 2.5 ppm and δ 2.0 ppm which may be attributed to products of the reaction of bismuthio methanide with acetonitrile.

The bismuthio methanides are readily hydrolysed in protonic solvents if any moisture is present. For example, $(C_6H_5)_3Bi{=}C(SO_2CF_3)_2$ is completely hydrolysed in acetonitrile solution containing 5% water within 15 min to finally give $(C_6H_5)_3BiO$ and $H_2C(SO_2CF_3)_2$ as described in eqn. (3).

The ^{19}F NMR spectrum of triphenylbismuthio bis(trifluoromethylsulfonyl)methanide exhibited a significant high-field shift of the CF_3 group as compared with the resonance of $H_2C(SO_2CF_3)_2$ (δ −81.78 ppm versus δ −76.46 ppm), indicating a higher electron density at the fluorine atoms. A reverse change in chemical shift was observed for the ^{13}C resonances of the CF_3 groups. The CF_3 group of $(C_6H_5)_3Bi{=}C(SO_2CF_3)_2$ exhibited a resonance at δ 122.21 ppm whereas that of $H_2C(SO_2CF_3)_2$ resonated at δ 119.89 ppm. The change in the chemical shifts of the methanide C atom was even more striking. The methanide resonance was shifted by *c*. 10 ppm to high field compared with methane (δ 54.69 ppm versus δ 65.31 ppm) and was located in the region of the methanide shifts of the phenyliodonio bis(nonafluorobutylsulfonyl)methanides [12]. This high-field shift indicates an increased electron density at the methanide carbon atom. In contrast to changes of the C-1 shifts of phenyliodinio ylides [15] but in agreement with changes of the C-1 shifts of triphenylphosphonio ylides [16], the C-1 resonance of the triphenylbismuthio derivative was shifted by *c*. 20 ppm upfield relative to those of triphenylbismuth and triphenylbismuth dihalides [17]. Similar effects were also found for the C_4F_9 and the $HCF_2CF_2CH_2O$ derivatives.

These results demonstrate that there is no evidence for the existence of a bismuth–carbon double bond. Canonical structures with a charge separation ($Bi^+{-}C^-$ or $Bi^+{-}C{=}S{-}O^-$) as discussed in refs. 8 and 9 must therefore be assumed to be most likely (see Fig. 1).

Experimental

Literature methods were used for the synthesis of $(C_6H_5)_3BiCl_2$ [18], $H_2C(SO_2CF_3)_2$ [19], $H_2C(SO_2C_4F_9)_2$ by analogy with ref. 19 and $H_2C(SO_2OCH_2CF_2CF_2H)_2$ [20]. All solvents were purified by recognised methods

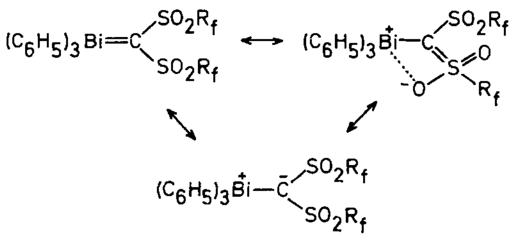

Fig. 1. Canonical structures for $(C_6H_5)_3Bi{=}C(SO_2R_f)_2$.

[21]. All compounds were handled in a dry N_2 atmosphere using Schlenk techniques.

^{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, ^1H NMR spectra on a Gemini 200 spectrometer, ^{13}C NMR spectra on a Bruker model AC 200 spectrometer (^{13}C, 50.3 MHz) with positive shifts being low field from the external standard CCl_3F (^{19}F) and internal standard TMS (^1H, ^{13}C).

The following NMR data were obtained for $H_2C(SO_2CF_3)_2$, $(C_6H_5)_3BiCl_2$ and $(C_6H_5)_3Bi$.

$H_2C(SO_2CF_3)_2$ (CD_3CN): ^{19}F: $\delta(CF_3)$ -76.46 [s, $^1J(^{19}F{-}^{13}C) = 326.7 \pm 0.2$ Hz]; $^1\Delta(^{12/13}C{-}^{19}F)$ 0.1316 ppm. ^1H: $\delta(CH_2)$ 5.82 (broad, $\Delta_{1/2} \approx 33$ Hz) ppm. $^{13}C\{^1H\}$: $\delta(CF_3)$ 119.89 [q, $^1J(^{19}F{-}^{13}C) = 326.8 \pm 0.2$ Hz]; $\delta(CH_2)$ 65.31 [sept, $^4J(^{19}F{-}^{13}C) = 1.6 \pm 0.2$ Hz] ppm [$^1J(^{13}C{-}^1H) \approx 150$ Hz, $\Delta_{1/2} \approx 40$ Hz determined from the ^1H coupled spectrum].

$(C_6H_5)_3BiCl_2$ (CD_3CN): $^{13}C\{^1H\}$: δ(C-1) 157.38; δ(C-2,6) 135.14; δ(C-3,5) 132.87; δ(C-4) 132.80 ppm.

$(C_6H_5)_3Bi$ (CD_3CN): $^{13}C\{^1H\}$: δ(C-1) 156.60 ($\Delta_{1/2} \approx$ 100 Hz); δ(C-2,6) 138.19; δ(C-3,5) 131.15; δ(C-4) 128.41 ppm.

Preparation of triphenylbismuthio bis(trifluoromethylsulfonyl)methanide

To a sodium methanolate solution, obtained from 34.5 mg (1.5 mmol) NaH in 2 ml CH_3OH, 210 mg (0.75 mmol) $H_2C(SO_2CF_3)_2$ was added. The reaction mixture was stirred for 10 min, CH_3OH distilled off *in vacuo* and the residue dried for 30 min under reduced pressure. CH_3CN (5 ml) was then added to the dry residue and 380 mg (0.75 mmol) $(C_6H_5)_3BiCl_2$ added to the resulting suspension. After stirring the reaction mixture for 30 min at ambient temperature, the precipitate (NaCl) was filtered off and washed with 5 ml CH_3CN. The solvent was evaporated and the remaining solid $(C_6H_5)_3Bi{=}C(SO_2CF_3)_2$ dried under reduced pressure at ambient temperature. $(C_6H_5)_3Bi{=}C(SO_2CF_3)_2$ was obtained as a white solid in 95% yield (500 mg), m.p. 108–110 °C (dec.). Elemental analysis for $C_{21}H_{15}BiF_6O_4S_2$ [Found (%) (Calc. (%))]: C, 35.22 (35.11); H, 2.48 (2.10); F, 15.75 (15.87). ^{19}F NMR (CD_2Cl_2): δ -81.78 (s) ppm. ^1H NMR (CD_2Cl_2): δ 7.35–7.72 (m, broad) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN): δ(C-1) 135.01; δ(C-2, 6) 132.62; δ(C-3,5) 132.47; δ(C-4) 135.43; $\delta(CF_3)$ 122.21 [q, $^1J(^{19}F{-}^{13}C) = 321.0$ Hz]; δ(methanide) 54.69 (m) ppm.

Preparation of triphenylbismuthio bis(nonafluorobutylsulfonyl)methanide

This compound was prepared according to the procedure mentioned above from 440 mg (0.76 mmol) $H_2C(SO_2C_4F_9)_2$ and 390 mg (0.76 mmol) $(C_6H_5)_3BiCl_2$. $(C_6H_5)_3Bi{=}C(SO_2C_4F_9)_2$ was obtained as a colourless solid in 95% yield (738 mg), m.p. 80–82 °C. Elemental analysis for $C_{27}H_{15}BiF_{18}O_4S_2$ [Found (%) (Calc. (%))]: C, 32.09 (31.84); H, 1.60 (1.48); F, 33.51 (33.58). ^{19}F NMR (CD_3CN): $\delta(CF_3)$ -81.2; $\delta(\alpha\text{-}CF_2)$ -114.4; $\delta(\beta\text{-}CF_2)$ -121.1; $\delta(\gamma\text{-}CF_2)$ -126.2 ppm. ^1H NMR ($CDCl_3$): δ 7.49–7.75 (m, broad) ppm.

Preparation of triphenylbismuthio bis(2,2,3,3-tetrafluoropropoxysulfonyl)methanide

According to the procedure given above, $(C_6H_5)_3Bi{=}C(SO_2OCH_2CF_2CF_2H)_2$ was prepared from 250 mg (0.62 mmol) $H_2C(SO_2OCH_2CF_2CF_2H)_2$ and 310 mg (0.61 mmol) $(C_6H_5)_3BiCl_2$ in 86% yield (510 mg), m.p. 148–149 °C (dec.). Elemental analysis for $C_{25}H_{21}BiF_8O_6S_2$ [Found (%) (Calc.)] C, 35.88 (35.64); H, 2.26 (2.51); F, 18.12 (18.04). ^{19}F NMR [$(CD_3)_2SO$]: $\delta(CF_2)$ -124.7; $\delta(CF_2H)$ -139.0 [$^2J(^{19}F{-}^1H) = 52$ Hz) ppm. ^1H NMR [$(CD_3)_2SO$]: $\delta(C_6H_5)$ 7.34–7.85 (m, broad, 15H); $\delta(CF_2H)$ 6.50 [tt, $^2J(^{19}F{-}^1H) = 52$ Hz, $^3J(^{19}F{-}^1H) = 5$ Hz, 2H]; $\delta(OCH_2)$ 4.27 [t, $^3J(^{19}F{-}^1H) = 14$ Hz, 4H] ppm.

Acknowledgements

Financial support by the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, the Fonds der Chemischen Industrie and the Ukrainian Committee of Science and Technology is gratefully acknowledged. S.V.P. thanks the Heinrich-Hertz-Stiftung for a grant. We thank Dr N.V. Pavlenko for the preparation of $H_2C(SO_2C_4F_9)_2$.

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