

The Reaction of Phenyliodonium Bis-(phenylsulfonyl)methylide with some Thiophenes

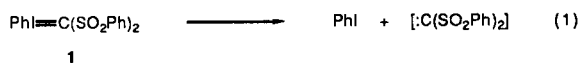
Lazaros Hatjiarapoglou and Anastasios Varvoglis*

Laboratory of Organic Chemistry, University of Thessaloniki,
Thessaloniki, 540 06 Greece
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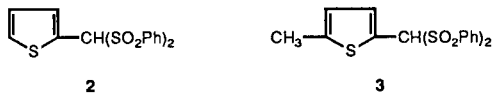
The title iodonium ylide gives with thiophenes C-H insertion products of the $C(SO_2Ph)_2$ group and with benzothiophenes transylidation products.

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Phenyliodonium bis(phenylsulfonyl)methylide, **1**, is a reactive and versatile ylide of hypervalent iodine with an interesting reactivity pattern [1]. Most of its reactions appear to involve generation of bis(phenylsulfonyl)carbene (or carbenoid) which gives with various substrates products containing initially the bis(phenylsulfonyl)methylene functionality. Thus **1** with alkenes, alkynes and thiobenzophenones gives under elimination of iodobenzene cycloaddition products (cyclopropanes or thiiranes) some of which are further transformed into indane or benzo[*b*]thiophene derivatives [2,3]. Non-charged nucleophiles containing S, N, P or As react with **1** to afford transylidation products [1]. Finally, benzene reacts also with **1** affording the insertion product phenyl bis(phenylsulfonyl)methane [1], $Ph-CH(SO_2Ph)_2$. Conditions favoring the heterolytic dissociation of **1** are either thermal, with catalysis by $Cu(acac)_2$ or photochemical (equation 1). In this communication reactions of **1** with some thiophenes are reported.



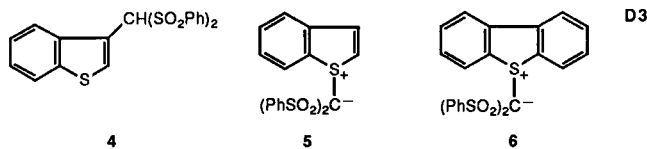
Thiophene and 2-methylthiophene reacted with **1** under photolytic conditions to afford, respectively, 2-bis(phenylsulfonyl)methyl derivatives **2** and **3**, as the sole thiophenic products.



The expected [4a] substitution at position 2- of the thiophene ring was confirmed from 1H nmr spectra. Both **2** and **3** had a singlet at δ 5.73 and 5.62, respectively, which was assigned to their methine proton of sp^3C ; further, **2** had a multiplet (1 H) centered at 6.97 and another multiplet (12 H) between 7.18 and 8.10, whereas **3** had one doublet at 6.87 (1 H) and a multiplet between 7.43-8.07 (11 H). Since mono-substituted thiophenes bearing an electron-withdrawing group (e.g. 2-nitrothiophene [4b]) show a high field absorption for their C-4 proton, it is reasonable to assume that the doublet of **3** is assigned to the C-4 proton (in 2-nitrothiophene C-4 proton resonates at 6.93 and

in 3-nitrothiophene at 7.56). Thus the 6.97 resonance of **2** must also pertain to the C-4 proton, since for thiophene itself the α -H resonates at 7.20 and the β -H at 6.96.

The reaction of **1** with benzo[*b*]thiophene gave a complex mixture of products photolytically but thermally after 1 hour reflux in chloroform a compound was isolated in low yield believed to have structure **4**. This showed a singlet at δ 5.73 in its 1H nmr spectrum (the methine proton) but all the other protons appeared as a multiplet (7.13-8.13). The structural assignment for **4** is not rigorous and it is mainly proposed based on the known tendency of benzo[*b*]thiophene to give 3-substituted products with electrophiles. When the reaction was repeated at a higher temperature without solvent, it was possible to isolate, besides some **4**, the ylide **5** as the main product in 28% yield. Other by-products in these reactions were bis(phenylsulfonyl)methane and phenyl benzenethiosulfonate, $Ph-SO_2SPh$, both obtained in most reactions of **1**.



That **5** is an ylide was corroborated by the absence of the sp^3CH resonance and a high field doublet at δ 6.87, assigned to the C-3 proton of the benzothiophene ring. Although isomeric with **4**, **5** has a completely different fragmentation pattern in its mass spectrum, its most prominent feature being the benzothiophene ion (base peak), which is absent in **4**.

Sulfur is nucleophilic enough even in dibenzothiophene, with which **1** gave the corresponding ylide **6**.

In conclusion, **1** reacts with the thiophene ring to afford two kinds of products, in which the bis(phenylsulfonyl)methylene group is either attached to sulfur or formally inserted into a C-H bond. From a mechanistic point of view two pathways are available for the formation of these compounds: either initial ylide formation, followed by rearrangement or cyclopropanation, also followed by rearrangement. Since it is unlikely that cyclopropane intermediates rearrange to ylides, whose formation is favored

at higher temperature, it is suggested that C-substitution follows the cyclopropane pathway. Analogous results have been reported for the reaction of thiophene with diazoketones and diazomalonic esters, where cyclopropanes have actually been isolated [5].

Several phenyliodonium ylides bearing two aryl or alkyl sulfonyl groups at the ylide carbon are presently available [2,3] and it should be expected that they react with thiophenes in a similar manner as **1**; this has already been substantiated [6] with the ylide $\text{PhI} = \text{C}(\text{SO}_2\text{Me})_2$.

EXPERIMENTAL

Phenyliodonium bis(phenylsulfonyl)methylide has been prepared according to our procedure, from diacetoxyiodobenzene and bis(phenylsulfonyl)methane [2]. The thiophenes were commercial samples and were used as received. The melting points were recorded on a Kofler hot-stage apparatus and are uncorrected. The ir spectra (in Nujol) were obtained with a Perkin-Elmer Model 297 spectrophotometer; ^1H nmr spectra were recorded on a Varian A-60A instrument in deuteriochloroform with TMS as internal standard; mass spectra were obtained with a Hitachi-Perkin-Elmer RMU-6L single focusing mass spectrometer at 70 eV. Elemental microanalyses were carried out in the analytical section of our laboratory. Column chromatography was carried out using silica gel and dichloromethane-light petroleum (40-60° bp fraction).

Reactions of **1** with Thiophene and 2-Methylthiophene.

A 0.5 g quantity (1 mmole) of **1** in either neat thiophene (15 ml) or in a solution of 2-methylthiophene (5 ml) in acetonitrile (10 ml) was irradiated in a Pyrex tube using a Philips 400 W low pressure mercury lamp (for 5 and 2 hours, respectively). After removal of volatiles column chromatography afforded iodobenzene and compounds **2** and **3**.

2-Bis(phenylsulfonyl)methylthiophene (**2**).

This compound was obtained in 56% yield as colorless crystals, mp 174-176° (chloroform-light petroleum); ir: 1350, 1165, 850 cm^{-1} ; nmr: δ 5.73 (s, 1H), 6.97 (m, 1H), 7.17-8.10 (m, 12H); ms: m/e 378 (M^+ , 2%), 237 (66%), 173 (25%), 125 (100%).

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{O}_4\text{S}_3$: C, 53.95; H, 3.73. Found: C, 53.98; H, 3.59.

Bis(phenylsulfonyl)methyl-5-methyl thiophene (**3**).

This compound was obtained in 38% yield as colorless crystals, mp 145-147° (chloroform-light petroleum); ir: 1355, 1175, 820 cm^{-1} ; nmr: δ 2.40 (s, 3H), 5.62 (s, 1H), 6.87 (d, 1H, $J = 4$ Hz), 7.43-8.07 (m, 11H); ms: m/e 392 (M^+ , 0.4%), 251 (15%), 141 (8%), 125 (100%).

Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_4\text{S}_3$: C, 55.08; H, 4.11. Found: C, 54.88; H, 3.99.

Reactions of **1** with Benzo[*b*]thiophene and Dibenzothiophene.

A 0.5 g quantity (1 mmole) of **1** and benzo[*b*]thiophene (0.7 g, 5.22 mmoles) or dibenzothiophene (0.368 g, 2 mmoles) was refluxed in dry chloroform (20 ml) in the presence of $\text{Cu}(\text{acac})_2$ (1 mg) under nitrogen for

1 or 1.5 hours (alternative conditions for benzo[*b*]thiophene: 0.5 g of **1**, 1 g of benzothiophene, 1 mg of $\text{Cu}(\text{acac})_2$, no solvent, heating under nitrogen at 90° for 15 minutes). After removal of volatiles, column chromatography afforded for benzo[*b*]thiophene in chloroform: iodobenzene, phenyl benzenethiosulfonate and **4** and for benzo[*b*]thiophene without solvent: iodobenzene, phenyl benzenethiosulfonate, **4**, bis(phenylsulfonyl)methane and **5**.

3-Bis(phenylsulfonyl)methylbenzo[*b*]thiophene (**4**).

This compound was obtained from the first reaction in 15% yield as colorless crystals, mp 229-231° (chloroform-light petroleum); ir: 1330, 1155, 855 cm^{-1} ; nmr: δ 5.73 (s, 1H), 7.13-8.13 (m, 15H); ms: m/e 428 (M^+ , 0.5%), 300 (1%), 287 (6%), 223 (9%), 222 (12%), 147 (18%), 125 (22%), 78 (100%).

Anal. Calcd. for $\text{C}_{21}\text{H}_{16}\text{O}_4\text{S}_3$: C, 58.86; H, 3.76. Found: C, 58.77; H, 3.67.

Benzo[*b*]thiophenium Bis(phenylsulfonyl)methylide (**5**).

This compound was obtained from the reaction without solvent in 28% yield as colorless crystals, mp 175-177° (chloroform-light petroleum); ir: 1320, 1145 cm^{-1} ; nmr: δ 6.87 (d, 1H, $J = 6$ Hz), 7.22-7.73 (m, 15H); ms: m/e 428 (M^+ , 0.2%), 376 (2%), 338 (2%), 287 (5%), 274 (16%), 250 (12%), 135 (20%), 134 (100%).

Anal. Calcd. for $\text{C}_{21}\text{H}_{16}\text{O}_4\text{S}_3$: C, 58.86; H, 3.76. Found: C, 58.50; H, 3.35.

In the reaction with dibenzothiophene the residue after removal of solvent was triturated with diethyl ether to give dibenzothiophenium bis(phenylsulfonyl)methylide (**6**) in 45% yield as colorless crystals, mp 212-214° (ethanol-benzene); ir: 1315, 1130 cm^{-1} ; nmr: δ 7.20-7.57 (m), 7.87-8.15 (m); ms: m/e 278 (1%), 216 (100%), 184 (72%), 171 (18%).

Anal. Calcd. for $\text{C}_{25}\text{H}_{18}\text{O}_4\text{S}_3$: C, 58.80; H, 3.55. Found: C, 59.08; H, 3.53.

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