SHORT PAPER

A novel synthesis of α-thio- and seleno-arsonium ylides *via* the mixed iodonium-arsonium ylides[†]

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The mixed iodonium-arsonium ylides **3**, which were prepared from arsonium ylides **1** and a mixture of PhI(OAc)$_2$ and HBF$_4$, reacted with MYAr (M=H, Na; Y=S, Se) to afford α-arylthio (or arylseleno) arsonium ylides **5**.

Ylides play an important role in the formation of carbon–carbon double bonds.[1] In particular, α-functionalised ylides can introduce many functional groups into alkene molecules through Wittig reaction. α-Functionalised arsonium ylides have more importance as Wittig reagents because of their higher reactivity than the corresponding phosphonium ylides, sulfonium ylides and α-carbanion of phosphonates.[2]

α-Functionalised arsonium ylides are usually synthesised through transylidation reactions.[2] This method affords a mixture of the desired arsonium ylide and arsonium salt, at least half of the starting arsonium ylide being lost by conversion to the arsonium salt. Moreover, the formed arsonium ylide and arsonium salt are usually difficult to separate. It seemed worthwhile to exploit a new method for the synthesis of α-functionalised arsonium ylides.

Considering that hypervalent iodine compounds have enjoyed much attention and become very useful in organic synthesis as synthons of cations,[3] in this paper we report a novel method for the synthesis of α-thio and seleno arsonium ylides through the substitution reaction of α-hypervalent iodine-substituted arsonium ylides.

α-Hypervalent iodine-substituted arsonium ylides **3** were generated in good yields by the reaction of the starting arsonium ylides **1** with PhI(OAc)$_2$ and HBF$_4$ in the dark. Although the ylides **3** could separate out as white solids from the reaction mixture, they were relatively unstable and could only be stored in the refrigerator for two days in the absence of light. A possible mechanism could be that the hypervalent iodine-type electrophile, PhI$^+$-OAc, generated by the reaction of PhI(OAc)$_2$ with HBF$_4$, attacks the α-carbon atom of the ylides **1** to form intermediate **2**, followed by the elimination of HOAc to produce α-hypervalent iodine-substituted arsonium ylides **3** (Scheme 1).[4]

α-Hypervalent iodine-substituted arsonium ylides **3** may be considered as iodonium-arsonium mixed ylides since the negative charge on the α-carbon of the ylides **3** is not only dispersed on the arsonium atom but also on the iodine atom (Scheme 2). To our best knowledge, this is the first example of iodonium–arsonium mixed ylides.

In general, the α-carbon of arsonium ylides possessed the stronger nucleophilic reactivity and can be attacked by an electrophilic reagent so that a transylidation reaction takes place. However, when the mixed ylides **3** were treated with nucleophiles, for example, MYAr (M=H, Na; Y=S, Se) in acetonitrile at 0°C, the substitution reaction took place (Scheme 3) to generate α-thio- and seleno-arsonium ylides **5** in good
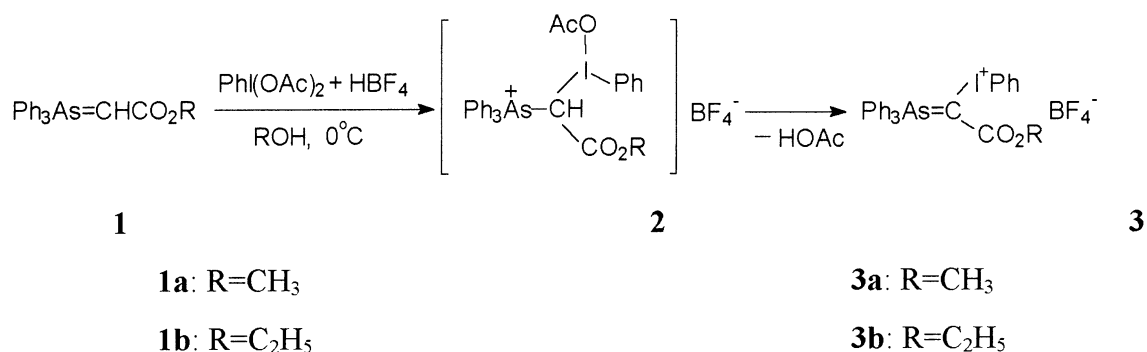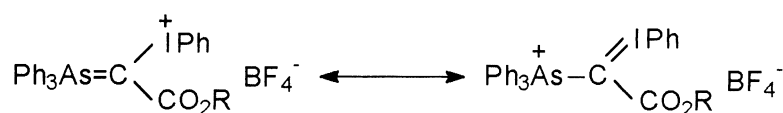
1

1a: R=CH$_3$

1b: R=C$_2$H$_5$

2

3

3a: R=CH$_3$

3b: R=C$_2$H$_5$

Scheme 1

Scheme 2

Table 1 Substitution reaction of the mixed ylides **5** with MYAr

Entry[a]	R	M	Y	Ar	M.p./°C	Yield/%
5a	CH_3	H	S	Ph	185–186	86
5b	CH_3	H	S	p-$CH_3C_6H_4$	168–169	83
5c	C_2H_5	H	S	Ph	174–175	85
5d	C_2H_5	H	S	p-$CH_3C_6H_4$	163–164	80
5e	CH_3	Na	Se	Ph	202–204[b]	70

[a]All new compounds were determined by ^1H NMR, MS, IR and elemental analysis.
[b]Lit.[2a] m.p. 203–205°C.
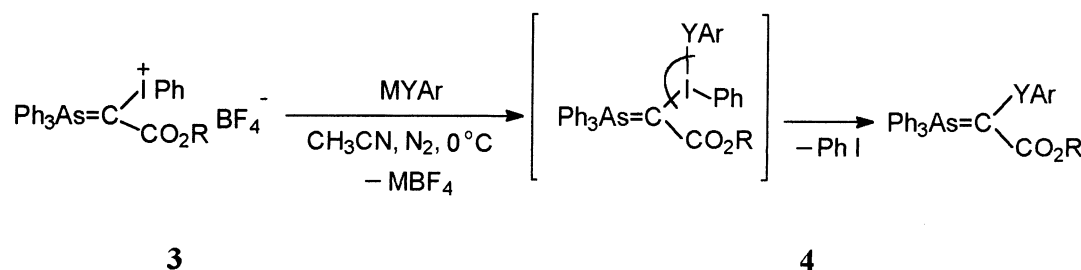
Scheme 3

yields. Therefore, the mixed ylides **3** are useful as synthons of cations on the α-position of arsoniun ylides. The results are compiled in Table 1.

A possible mechanism[5] on this substitution reaction is that nucleophiles, ArY⁻, first coordinate with the central iodine atom of the mixed ylides **3** to form hypervalent iodine intermediates **4**, followed by ligand ArY coupling to the α-carbon of the mixed ylides **3** and simultaneous elimination of PhI to produce α-thio- and seleno-arsonium ylides **5**.

The advantages of this new method are simple operation, mild conditions and good yields. In particular, only one molecule of the starting arsonium ylide **1** is consumed, this avoiding the cumbersome separation between the α-functionalised arsonium ylides and the arsonium salts formed.

In summary, we have synthesised the first example of mixed iodonium-arsonium ylides **4** and exploit a novel method for the synthesis of α-thio- or α-seleno-arsonium ylides through a substitution reaction instead of the usual transylidation reaction.

Experimental

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on JEOL PMX60SI (60MHz) with TMS as internal standard. Infrared (IR) spectra were obtained as KBr disks on a PE 683 instrument. Mass spectra data were obtained by electron ionisation (EI) on a HP 5989A mass spectrometer.

Melting points were uncorrected. Methoxycarbonylmethylene triphenylarsorane **1a** and ethoxycarbonylmethylene triphenylarsorane **1b** were prepared according to literature.[6]

Preparation of the mixed iodonium-arsonium ylides **3a** *(typical procedure):* A mixture of 1mmol (0.32 g) PhI(OAc) and 1 mmol (1.1 N, 0.09 ml) HBF₄ in 1 ml of methanol was dropwise added to the solution of 1 mmol (0.38 g) methoxycarbonylmethylene triphenylarsorane in 0.6 ml of methanol at 0°C when light was prevented. After stirring for 3h, 1.5 ml of diethyl ether was added to the reaction mixture. The mixture was laid up for 2 hrs below 0°C, then filtered to afford **3a** as a white solid (0.47 g, 70%), m.p. 109–111°C (dec.) (Found: C, 48.45. H, 3.58; I, 18.79. $C_{27}H_{23}AsBF_4IO_2$ requires C, 48.54; H, 3.47; I, 18.99%); δ_H 7.62–7.54 (20H, m), 3.67 (3H, s); ν_{max} (KBr)/cm⁻¹ 1600, 1445, 1310, 1060, 740, 690.

The compound **3b** (0.56 g, 82%), m.p. 108–110 °C (dec.) (Found: C, 49.21; H, 3.59; I, 18.70. $C_{28}H_{25}AsBFIO_2$ requires C, 49.30; H, 3.69; I, 18.60%); δ_H 7.70–7.40 (20H, m), 4.06 (2H, q, J 7Hz), 1.03 (3H, t, J 7Hz); ν_{max} (KBr)/cm⁻¹ 1600, 1450, 1290, 1055, 740, 685.

Preparation of α-functionallised arsonium ylides **5b** *(typical procedure):* A solution of 1 mmol (0.11 g) p-$CH_3C_6H_4SH$ in 1.5 ml of acetonitrile was dropwise added to a mixture of 1mmol (0.67 g) the mixed ylide **3a** and 1 mmol (0.14 g) anhydrous potassium carbonate

in 3 ml of acetonitrile at 0°C under nitrogen when light was prevented. After stirring 4h, acetonitrile was removed under reduced pressure, then 15 ml of benzene was added. After filtration, benzene in filtrate was removed under reduced pressure, then washed with few amount of diethyl ether to afford white solid. The white solid was recrystallised from methanol to give pure compound **5b** (Found: 67.10; H, 5.09. $C_{28}H_{25}AsO_2S$ requires C, 67.20; H, 5.03%); δ_H 7.49–7.02 (19H, m), 3.69 (3H, s), 2.24 (3H, s); ν_{max} (KBr)/cm⁻¹ 1605, 1490, 1450, 1280, 1080, 805, 740, 690; m/z 500 (M⁺, 2%), 306 (57), 227 (31), 152 (100), 91 (7), 77 (13).

Compound **5a** (Found: C, 66.49; H, 4.89. $C_{27}H_{23}AsO_2S$ requires C, 66.67; H, 4.77%); δ_H 7.37–7.07 (20H, m), 3.63 (3H, s); ν_{max} (KBr)/cm⁻¹ 1600, 1485, 1300, 760, 720; m/z 486 (M⁺, 24%), 306 (14), 227 (36), 152 (100), 109 (8), 77 (7).

Compound **5c** (Found: C, 67.17; H, 4.93. $C_{28}H_{25}AsO_2S$ requires C, 67.20; H, 5.03%); δ_H 7.65–7.13 (20H, m), 4.07 (2H, q, J 7Hz), 1.07 (3H, t, J 7Hz); ν_{max} (KBr)/cm⁻¹ 1610, 1485, 1445, 1280, 740, 680; m/z 500 (M⁺, 10%), 306 (18), 227 (33), 152 (100), 77 (10).

Compound **5d** (Found: C, 67.40; H, 5.51. $C_{29}H_{27}AsO_2S$ requires C, 67.70; H, 5.29%); δ_H 7.66–6.81 (19H, m), 3.94 (2H, q, J 7Hz), 2.11 (3H, s), 0.98 (3H, t, J 7Hz); ν_{max} (KBr)/cm⁻¹ 1605, 1500, 1445, 1290, 1185, 800, 745, 690; m/z 514 (M⁺, 11%), 416 (32), 306 (74), 229 (39), 152 (100), 135 13), 91 (11), 77 (15).

Compound[2a] **5e**; δ_H 7.70–7.09 (20H, m), 3.41 (3H, s); ν_{max} (KBr)/cm⁻¹ 1600, 1445, 1300,750, 695.

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