

## An Improved Synthesis of $\alpha$ -Phenylseleno Arsonium Ylides

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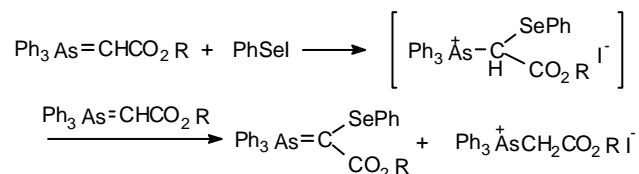
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**Abstract:**  $\alpha$ -Seleno arsonium ylides **5** have been synthesized through the reaction of  $\alpha$ -unfunctionalized arsonium ylides **4** with almost equimolar phenylselenenyl iodide **2**.

**Keyword:** Synthesis, ylide,  $\alpha$ -seleno arsonium ylide.

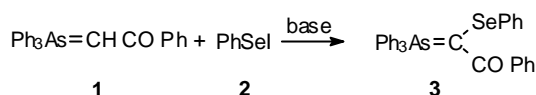
The first  $\alpha$ -seleno arsonium ylides have been synthesized by phenylselenenylation-transylidation<sup>1, 2</sup>. It has been found that they can converse into  $\alpha$ -phenylseleno- $\alpha$ ,  $\beta$ -unsaturated compounds through their Wittig-type reactions in good yield<sup>1, 2</sup>. Therefore these Wittig reagents become useful intermediate in organic synthesis.  $\alpha$ -Seleno arsonium ylides were prepared by the treatment of  $\alpha$ -unfunctionalized arsonium ylides with phenylselenenyl iodide to afford an equimolar mixture of the desired  $\alpha$ -seleno arsonium ylide and arsonium salt (**Scheme A**)<sup>1, 2</sup>. Therefore at least half of the starting arsonane was converted to undesired arsonium salt.

### Scheme A



We have found that  $\alpha$ -seleno arsonium ylides **3** can be obtained in excellent yield when  $\alpha$ -unfunctionalized arsonium ylides **1** are treated with almost equimolar phenylselenenyl iodide **2** in the presence of weak base such as potassium carbonate, sodium acetate and triethylamine (**Scheme B**). The results are list in **Table 1**.

### Scheme B

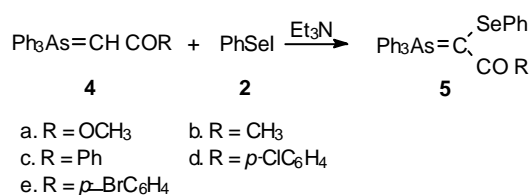


Among them, triethylamine is better. So other unfunctionalized arsonium ylides **4** are treated with almost equimolar phenylselenenyl iodide **2** in the presence of triethylamine to provide  $\alpha$ -seleno arsonium ylides **5** in good yield as well (**Scheme C**). The results are compiled in **Table 2**.

**Table 1.** Yield of  $\alpha$ -Seleno Arsonium Ylide **3** in the Presence of Base

Entry	Base	Yield (%)
<b>3a</b>	CH <sub>3</sub> COONa	86
<b>3b</b>	K <sub>2</sub> CO <sub>3</sub>	80
<b>3c</b>	Et <sub>3</sub> N	90

The ratio of **1**, **2** and base is equal to 1:0.85:1.1.

**Scheme C****Table 2.** An improved synthesis of  $\alpha$ -seleno arsonium ylids **5**

Entry <sup>a</sup>	R	mp. (°C)	Yield (%)
<b>5a</b>	OCH <sub>3</sub>	202-204 <sup>b</sup>	80
<b>5b</b>	CH <sub>3</sub>	180 (decompd.) <sup>c</sup>	83
<b>5c</b>	Ph	197-199 <sup>d</sup>	90
<b>5d</b>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	180-182 <sup>e</sup>	90
<b>5e</b>	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	173-176 <sup>e</sup>	89

a) The ratio of **4**, **2** and Et<sub>3</sub>N is equal to 1:0.85:1.1. b) lit<sup>1</sup>. 203-205 °C. c) lit<sup>2</sup>. 180 °C (decompd.). d) lit<sup>2</sup>. 198-200 °C. e) All compounds were confirmed by <sup>1</sup>H NMR, IR, MS and elemental analysis.

Typical procedure for the synthesis of compound **5a**. To a stirred suspension of methoxycarbonylmethylene triphenylarsorane (**4a**) (0.378 g, 1 mmol) and triethylamine (0.11 g, 1.1 mmol) in MeOH-Et<sub>2</sub>O (0.6 ml, v/v=1:1) was added dropwise the solution of phenylselenenyl iodide **2** (0.85 mmol) in MeOH-Et<sub>2</sub>O (2.8 ml, v/v=1:1) at 0 °C for 14 hrs. The mixture was stirred again for 6 hrs. After the solvent in the mixture was evaporated under reduced pressure, the residue was washed with water, then with ether, finally recrystallized from ethanol to provide the compound **5a** in 80% yield, mp. 202-204 °C (lit<sup>1</sup>. 203-205 °C), <sup>1</sup>H NMR (60 MHz, CDCl<sub>3</sub>, TMS)  $\delta$  ppm: 7.70-7.09 (20H, m), 3.41 (3H, s). IR (KBr) cm<sup>-1</sup>: 1600(s), 1445(vs), 1300(s), 750(s), 695(s).

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**References**

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