

## A Facile Synthesis of $\alpha$ -Phenylthio- $\alpha$ , $\beta$ -Unsaturated Esters

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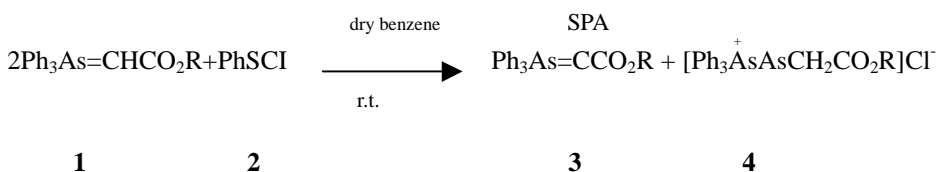
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**Abstract:**  $\alpha$ -Phenylthio- $\alpha$ ,  $\beta$ -unsaturated esters **6** were synthesized by Wittig reaction of **3**, which were prepared by a phenylsulfenylation-trans-ylidation reaction.

**Keywords:** Wittig reaction, arsonium ylides, unsaturated esters, synthesis.

$\alpha$ -Phenylthio- $\alpha$ , $\beta$ -unsaturated esters **6** are in great demand as Michael acceptors<sup>1</sup>, Diels-Alder dienophiles<sup>2</sup>. Many methods toward their synthesis have been described so far<sup>1, 3-7</sup>. However, these methods are deficient in some respects, such as low yields, multistep sequence or severe reaction condition. In recent years, chemists are interest in the synthesis of  $\alpha$ -functionalize arsonium ylides, but also the functionalize groups can be introduced on the  $\alpha$ -position of  $\alpha$ ,  $\beta$ -unsaturated compounds through their Wittig reaction. Based upon our previous experience<sup>8-12</sup>, these compounds can be synthesized concisely and efficiently through Wittig reaction of the corresponding arsonium ylides, but difficultly by the corresponding phosphonium ylides due to their poor activity<sup>13</sup>. In this letter, we describe the preparation of  $\alpha$ -phenylthio- $\alpha$ ,  $\beta$ -unsaturated esters **6** through  $\alpha$ -phenylthio alkoxy carbonylmethylene triphenylarsoranes **3**.

### Scheme A



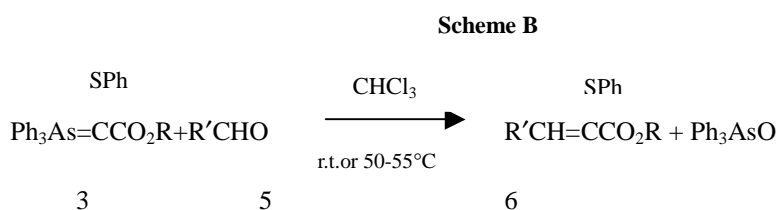
a, R=CH<sub>3</sub>; b, R=C<sub>2</sub>H<sub>5</sub>

Ylides **3**<sup>14</sup> were almost quantitatively synthesized through the *trans*-ylidation reaction of alkoxy carbonylmethylene triphenylarsoranes **1** (2 equiv.), which were synthesized according to the literature<sup>15</sup>, with phenylsulfenyl chloride **2**<sup>16,17</sup> (1 equiv.) in benzene at room temperature (**Scheme A**), m.p. 185-186°C (**3a**, R=CH<sub>3</sub>), 174-175°C (**3b**,

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R=C<sub>2</sub>H<sub>5</sub>) and confirmed by <sup>1</sup>H NMR, MS, IR and elemental analysis.

As expected, Ylides **3** can undergo Wittig reaction with a great diversity of aromatic and aliphatic aldehydes **5** under mild condition to afford (*z*)-  $\alpha$ -phenylthio- $\alpha$ ,  $\beta$ -unsaturated esters **6** as dominant products in good yields<sup>18</sup> (**Scheme B**). The results were listed in **Table 1**.



**Table 1** Wittig-type reaction between  $\alpha$ -phenylthio alkoxy-carbonylmethylene triphenylarsorane **3** and aldehydes **5**

Entry	R'	R	Reaction	Reaction Temperature(°C)	Yield(%) <sup>a</sup>	Z/E <sup>b</sup>
<b>6a<sup>c</sup></b>	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	Me	5	10	99	95/5
<b>6b<sup>c</sup></b>	Ph	Me	13	50	97	75/25
<b>6c<sup>d</sup></b>	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	Me	12	50	98	70/30
<b>6d<sup>e</sup></b>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	Me	24	50	78	100/0
<b>6e<sup>c</sup></b>	Ph	Et	25	10	84	75/25
<b>6f<sup>c</sup></b>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	Et	24	50	75	95/5
<b>6g<sup>e</sup></b>	<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	Et	7	8	91	90/10

### Acknowledgments

Project 29502006 was supported by the National Natural Science Foundation of China.

### References and Notes

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- A solution of phenylsulfenyl chloride **2** (11 mmol) in 50 mL dry benzene was added dropwise to a stirred solution of methoxycarbonylmethylene triphenylene **1a** (22 mmol) in 250 mL dry benzene at 11 for 2 hour. After the suspension was filtrated, the residue was reduced pressure and recrystallized in EtoH to give 4.93 g  $\alpha$ -phenylthio methoxy-carbonylmethylene

triphenylarsorane **3a** in 92 % yield as white crystal, m.p.185-186°C,  $^1\text{H}$ NMR (60 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 7.37-7.07(m, 20 H) and 3.63 (s, 3H);  $m/z$  486 ( $\text{M}^+$ , 23.76 %) and 152 (100.00); IR (KBr) v: 1600 (vs), 1485 (s), 1300 (vs), 760 (s), 720(s) $\text{cm}^{-1}$ . Anal. Calcd. For  $\text{C}_{27}\text{H}_{23}\text{AsO}_2\text{S}$ : C, 66.67; H, 4.77, Found: C67.19; H 4.65.

It was similar to the above procedure to rescue the arsonium salt **4b** in 93%, and obtain **3b** in 91% yield as white crystal, m. p. 174-175°C,  $^1\text{H}$  NMR (60 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm): 7.83-7.13 (m, 20H), 1.07 (t, 3H,  $J=7\text{Hz}$ );  $m/z$  500( $\text{M}^+$ ) and (100.00); IR (KBr) v: 1610(vs), 1485 (s), 1445 (s), 1280(vs), 740 (vs), 680 (vs) $\text{cm}^{-1}$ . Ana. Calcd. For  $\text{C}_{28}\text{H}_{25}\text{AsO}_2\text{S}$ : C, 67.20; H, 5.03. Found: C, 67.17; H, 4.93.

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18. The mixture of  $\alpha$ -phenylthio alkoxy carbonylthylene triphenylarsorane **3a** (1mmol) and *p*-nitrobenzaldehyde **5a** (0.9 mmol) in chloroform (2 mL) was stirred under  $\text{N}_2$  atmosphere for 5 h. The progress of reaction was examined by TLC. After finishing the reaction, the mixture of reaction was concentrated, and separated by flash chromatograph over silica gel (eluant 4:1 light petrol ether (30-60°C) diethyl ether ) to afford the *Z* and *E* isomer of **6a**. m. p. 54-61°C.  $^1\text{H}$ NMR (60 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  (ppm):7.90-7.75 (m, 2H), 8.07 (*Z*), 6.78 (*E*) (s,  $Z+E=1\text{H}$ ), 7.37-7.20 (m 5H), 3.67 (*Z*), 3.54 (*E*) (s,  $Z+E=3\text{H}$ ). IR (KBr) v:1730(vs), 1620 (s), 1530 (vs) ( $\text{NO}_2$ ), 1350 (vs), 1250 (vs), 850 (s), 730 (s), 690(s)  $\text{cm}^{-1}$ .

Received 12 March, 2002