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## Synthesis of $\alpha$ -Phenylseleno Carbomethoxymethylene Triphenylarsorane and Its Wittig Type Reaction

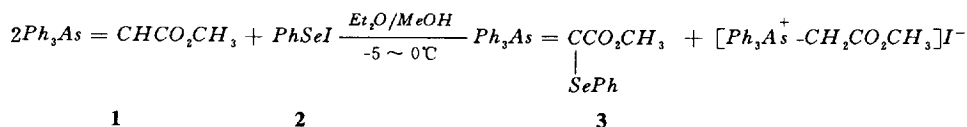
Zhi-Zhen Huang<sup>a</sup>, Xian Huang<sup>a</sup>, Yao-Zeng Huang<sup>b\*</sup>

<sup>a</sup>Department of Chemistry, Hangzhou University, Hangzhou, 310028, China  
<sup>b</sup>Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai, 200032, China

**Abstract:** The first example of  $\alpha$ -seleno arsonium ylide (**3**) was reported. It has sufficient activity to undergo a Wittig type reaction, affording a novel method for the stereoselective synthesis of (Z)- $\alpha$ -seleno- $\alpha,\beta$ -unsaturated compounds (**5**).

It is well known that ylides are one of the most widely used intermediates and organoselenium compounds are playing increasingly important roles in organic synthesis. Thus, introducing organoselenium compounds into ylides is undoubtedly very significant. Although  $\alpha$ -seleno phosphonium ylides were synthesized, it was found that  $\alpha$ -seleno  $\alpha$ -electron attracting group substituted phosphonium ylides cannot undergo a Wittig reaction.<sup>1,2</sup> These  $\alpha$ -seleno phosphonium ylides are stabilized due to the carbonyl conjugation and the orbital overlap of  $\alpha$ -carbon with selenium and are consequently unreactive towards aldehydes, which restricts its application in organic synthesis. Furthermore, the  $\alpha$ -carbanion of phosphonate is more reactive than the corresponding phosphonium ylide, but  $\alpha$ -seleno  $\alpha$ -electron attracting group substituted phosphonate also cannot undergo Horner-Emmons reaction.<sup>3</sup> Huang reported that the reactivity of arsonium ylides is higher than that of the corresponding phosphonium ylide and  $\alpha$ -carbanion of phosphonates.<sup>4</sup> Therefore, we started to synthesize  $\alpha$ -phenylseleno carbomethoxymethylene triphenylarsorane and tried to explore its Wittig type reaction.

We found that carbomethoxymethylene triphenylarsorane (**1**) can undergo transylidation reaction smoothly with phenylselenenyl iodide (**2**), prepared *in situ* by reacting diphenyl diselenide with iodine. At  $-5 \sim 0^\circ\text{C}$ , adding dropwise a solution of phenylselenenyl iodide (**2**, 1mol) in  $\text{Et}_2\text{O}-\text{MeOH}$  (1 : 1, 2.8ml) into the suspension of arsonium ylide (**1**, 2mmol) in  $\text{Et}_2\text{O}-\text{MeOH}$  (1 : 1, 0.6ml) gives  $\alpha$ -phenylseleno carbomethoxymethylene triphenylarsorane in excellent yield (93%). This is the first example of  $\alpha$ -seleno arsonium ylide. The white crystalline  $\alpha$ -seleno arsonium ylide (**3**) is relatively stable and has a mp of  $203 \sim 205^\circ\text{C}$ .



As expected, the  $\alpha$ -seleno arsonium ylide (**3**) is different from  $\alpha$ -seleno  $\alpha$ -electron-attracting group substituted phosphonium ylides or phosphonates in that it has sufficient activity to undergo a Wittig type reaction. It can react with aromatic aldehyde at room temperature or with aliphatic or  $\alpha,\beta$ -unsaturated aldehyde at 50~60°C. Stirring the mixture of  $\alpha$ -seleno arsonium ylide (**3**, 1.2mmol) with aldehydes (**4**, 1.0mmol) in chloroform (3ml) under nitrogen, a new type of vinyl selenides,  $\alpha$ -phenylseleno  $\alpha,\beta$ -unsaturated esters (**5**) can be obtained in excellent yields.  $\alpha$ -Seleno arsonium ylide (**3**) can also react *in situ* with aldehydes as a one-pot reaction, obtaining similar results. This Wittig type reaction has high stereoselectivity and provides the first method for the stereoselective synthesis of Z-type of  $\alpha$ -seleno- $\alpha,\beta$ -unsaturated compounds (**5**). The stereochemistry of this reaction is analogous to that of the Wittig type reaction of  $\alpha$ -iodo-carbomethoxymethylene triphenylarsorane.<sup>6</sup> The configuration of the product (**5**) was determined by 300MHz <sup>1</sup>H-NMR. This Wittig typed reaction has the advantages of mild conditions, simple manipulations, excellent yields and high stereoselectivities. The research on other  $\alpha$ -seleno substituted arsonium ylides is now in progress in our laboratory.

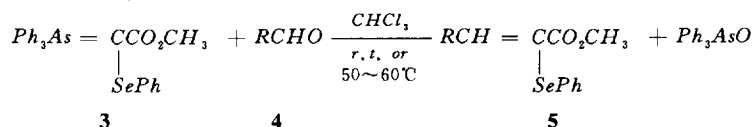


Table. The Wittig type reaction undergone by  $\alpha$ -seleno arsonium ylide (**3**).

| No. | R <sup>a</sup>  | Time(hr. ) | Yield(%) | $\delta_Z, \delta_E$ (ppm) <sup>b</sup> | Z/E <sup>c</sup> |
|-----|---|------------|----------|---|------------------|
| 5a  | P-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -                 | 4          | 96       | 8.07 6.84                               | 90/10            |
| 5b  | P-Cl C <sub>6</sub> H <sub>4</sub> -                              | 9          | 93       | 8.08 6.95                               | 84/16            |
| 5c  | C <sub>6</sub> H <sub>5</sub> -                                   | 16         | 98       | 8.18 7.08                               | 82/18            |
| 5d  | P-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -                 | 24         | 95       | 8.20 7.13                               | 81/19            |
| 5e  | C <sub>6</sub> H <sub>5</sub> CH=CH-                              | 15         | 93       | 8.15 7.1                                | 95/5             |
| 5f  | CH <sub>3</sub> -CH=CH-   | 18         | 90       | 7.75 6.6                                | 98/2             |
| 5g  | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>2</sub> - | 24         | 86       | 7.40 6.3                                | 99/1             |
| 5h  | (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> -               | 21         | 91       | 7.35 6.3                                | 99/1             |

a. All compounds were confirmed by <sup>1</sup>H-NMR, IR, MS and elemental analysis.

b. The chemical shift of olefinic proton of Z-isomer or E-isomer.

c. The ratio of Z-isomer to E-isomer was estimated by <sup>1</sup>H-NMR or GC.

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