## Synthesis of Acyl(phenylselanyl)methylidene(triphenyl)- $\lambda^5$ -arsanes and their Wittig-type Reactions

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

² Department of Ĉhemistry, Hangzhou University, Hangzhou, 310028, China º Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai, 200032, China

Acyl(phenylselanyl)methylidene(triphenyl)- $\lambda^5$ -arsanes **3** have been synthesized by treating acylmethylidene(triphenyl)- $\lambda^5$ -arsanes **1** with phenylselanyl iodide **2**;  $\alpha$ -selanylarsonium ylides **3** are sufficiently reactive to undergo Wittig-type reactions, affording a novel method for the stereoselective synthesis of (*Z*)- $\alpha$ -phenylselanyl  $\alpha$ , $\beta$ -unsaturated ketones **6**.

Ylides are among the most widely used intermediates in organic synthesis and organoselenium compounds are playing an increasingly important role.<sup>1</sup> Thus, it is of interest to introduce an organoselenium group into an ylide. Recently a-selanylphosphonium ylides have been synthesized,<sup>2</sup> however, it was found that the a-selanyl group rendered the ylides too unreactive to undergo Wittig olefination.<sup>3</sup> Although a-carbanions of phosphonates are more reactive than the corresponding phosphonium ylides, the  $\alpha$ -selanyl group also rendered these ylides too unreactive to undergo the Horner-Wadsworth-Emmons reaction.<sup>4</sup> The inactivity of these  $\alpha$ -selanylphosphonium ylides and  $\alpha$ -carbanions of phosphonates is mainly due to an orbital overlap between the a-carbanion and the selenium. Since arsonium ylides are more reactive than the corresponding phosphonium ylides and  $\alpha$ -carbanions of phosphonates,<sup>5</sup> we have synthesized acyl(phenylselanyl)methylidene(triphenyl)- $\lambda^5$ -arsanes and studied their Wittig-type reactions.

To date there is no literature on the synthesis of  $\alpha$ -selanylarsonium ylides. As arsonium ylides are strong nucleophiles and phenylselanyl halides are good electrophiles, we treated acylmethylidene(triphenyl)- $\lambda^5$ -arsanes 1 with phenylselanyl halides and found that a transylidation reaction took place. Of the phenylselanyl halides tested, phenylselanyl chloride, phenylselanyl bromide and 'phenylselanyl iodide' prepared in situ,<sup>6</sup> the last was the most reactive. Thus, in diethyl ether-methanol, acylmethylidene(triphenyl)- $\lambda^5$ -arsanes 1 (2 equiv.) react with phenylselanyl iodide 2 smoothly to produce acyl(phenylselanyl)methylidene(triphenyl)- $\lambda^5$ -arsanes 3a and 3b in 82% and 84% yield, respectively. The arsonium salts 4, which can be recycled, were formed almost quantitatively through the transylidation reaction. The white crystalline acetyl(phenylselanyl)methylidene(triphenyl)- $\lambda^5$ -arsane 3a decomposes at 180 °C and benzoyl(phenylseleno)methylidene(triphenyl- $\lambda^5$ -arsane 3b has a melting point of 198-200 °C. Although acyl(phenylselanyl)methylidene(triphenyl)- $\lambda^{5}$ -arsanes 3 are sensitive to heat, light and moisture, it is possible to store them for use in subsequent reactions.

$$2Ph_{3}As=CHCOR + PhSeI \xrightarrow{Et_{2}O-MeOH}_{room \ temp.}$$

$$1 \qquad 2$$

$$Ph_{3}As=CCOR + [Ph_{3}As=CH_{2}COR]I^{-1}$$

$$i \qquad 4$$

$$SePh \qquad 3$$

As expected, the acyl(phenylselanyl)methylidene(triphenyl)- $\lambda^{5}$ -arsanes 3 are more reactive than the corresponding phosphonium species and they have sufficient activity to undergo Wittig-type reactions. Both ylides 3a and 3b react with aromatic, aliphatic and  $\alpha,\beta$ -unsaturated aldehydes to produce  $\alpha$ -

Table 1	Wittig-type re	actions of	a-selanvl	arsonium	vlides 3 <sup>a</sup>
					J

			•	-	
Compound	R'	n	R	Yield (%)	$Z: E^b$
6a	m-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	0	Me	80	90:10
6Ъ	Ph	0	Me	75	75:25
6c	p-MeC <sub>6</sub> H₄	0	Me	65	70:30
6d	Ph	1	Me	81	91:9
бе	Me	1	Me	76	90:10
6f	Bu <sup>i</sup>	0	Me	61	80:20
бд	$p-NO_2C_6H_4$	0	Ph	80	85:15
6h	Ph	1	Ph	81	92:8
6i	Bu <sup>i</sup>	0	Ph	70	85:15
6j	Me	1	Ph	72	91:9

<sup>a</sup> The structures of all compounds were confirmed by <sup>1</sup>H NMR, IR, and mass spectroscopy and elemental analysis. <sup>b</sup> The ratio of Z- to Eisomer was estimated by <sup>1</sup>H NMR spectroscopy or GC.

phenylselanyl  $\alpha,\beta$ -unsaturated ketones 6 in good yields. Olefins 6 are a new type of vinyl selenide that are important intermediates for organic synthesis owing to the versatile reactivity of the organoseleno group.<sup>7</sup> It is not necessary to isolate the intermediate ylides 3; they can be treated *in situ* with aldehydes in a one-pot reaction, giving similar results. These Wittig-type reactions show good stereoselectivity and provide the first method for the stereoselective synthesis of (Z)- $\alpha$ -selanyl  $\alpha,\beta$ -unsaturated ketones 6. The stereochemistry of this reaction is analogous to that observed in the Wittig-type reactions of  $\alpha$ -iodoarsonium ylides.<sup>8</sup>

Research on other  $\alpha$ -organoselanylarsonium ylides is now in progress.

Ph<sub>3</sub>As=CCOR + R'(CH=CH)<sub>n</sub>CHO 
$$\xrightarrow{CHCl_3}{55-65 \circ C}$$
  
SePh  
3 5 R'(CH=CH)<sub>n</sub>CH=CCOR  
SePh  
6

## Experimental

General Procedure for the Synthesis of Acetyl(phenylselanyl)methylidene(triphenyl)- $\lambda^5$ -arsane 3a.—A solution of phenylselanyl iodide 2 (1 mmol), prepared *in situ* by treating diphenyl diselenide (0.156 g, 0.5 mmol) with iodine (0.127 g, 0.5 mmol) in Et<sub>2</sub>O-MeOH (5 cm<sup>3</sup>, 15:1 v/v), under nitrogen was added dropwise to a stirred suspension of acetylmethylidene-(triphenyl)- $\lambda^5$ -arsane 1a (0.724 g, 2 mmol) in Et<sub>2</sub>O-MeOH (3 cm<sup>3</sup>, 15:1 v/v) during 2 h. The reaction mixture was stirred at room temp. for a further 0.5 h and then diethyl ether (20 cm<sup>3</sup>) was added to it. After filtration the residue was washed with diethyl ether (10 cm<sup>3</sup> × 2) and then extracted with warm benzene (10 cm<sup>3</sup> × 3). Filtration gave a powdery residue, which was washed with tetrahydrofuran (THF) (10 cm<sup>3</sup> × 2) to yield the arsonium salt **4a** (0.47 g, 96%). The filtrate was evaporated under reduced pressure to give the *title compound* **3c** (0.42 g, 82%) as white crystals,  $\delta_{\rm H}$  7.85–7.05 (m, 20 H) and 2.34 (s, 3 H); *m/e* 518 (M, 5.88%) and 78 (100.00);  $\nu$  cm<sup>-1</sup>, 1570s, 1500vs, 745vs and 685s (Found: C, 62.1; H, 4.5. Calc. for C<sub>27</sub>H<sub>23</sub>AsOSe: C, 62.28; H, 4.48%).

Typical Procedure for the Synthesis of 4-Phenyl-3-phenylselanylbut-3-en-2-one **6b**.—A mixture of acetyl(phenylselanyl)methylidene(triphenyl)- $\lambda^5$ -arsane **3a** (0.776 g, 1.5 mmol) and benzaldehyde **5b** (0.106 g, 1 mmol) in chloroform (3 cm<sup>3</sup>) in the dark was stirred at 55–65 °C for 7 days under a N<sub>2</sub> atmosphere. When the reaction was complete (monitored by TLC), the mixture was concentrated and then subjected to flash chromatography on a silica gel column (light petroleum-diethyl ether, 5:1). The eluent was concentrated and the oil obtained was subjected to a preparative TLC (light petroleum-dichloromethane, 5:3) to yield the *title compound* **6b** (0.23 g, 75%);  $\delta_{\rm H}$ 7.97 (s, 0.75 H, Z-4-H), 7.85–6.70 (m, 10.25 H, 2 of C<sub>6</sub>H<sub>5</sub> + *E*-4-H), 2.34 (s, 0.75 H, Z-CH<sub>3</sub>) and 2.07 (s, 0.25 H, Z-CH<sub>3</sub>); *m*/z 302 (M, 22.62%) and 43 (100.00); v cm<sup>-1</sup> 1675vs, 1605s, 734vs and 685s (Found: C, 63.8; H, 4.7. Calc. for C<sub>16</sub>H<sub>14</sub>OSe: C, 63.79; H, 4.68).

## Acknowledgements

We thank the National Natural Science Foundation of China

and the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Academia Sinica, for their financial support.

## References

- 1 D. Liotta, Acc. Chem. Res., 1984, 17, 28.
- 2 (a) L. Braga, J. V. Comasseto and N. Petragnani, Synthesis, 1984, 240;
  (b) L. Wang, Z. Z. Huang, H. Li and X. Huang, Org. Prep. Proced. Int., 1994, in the press.
- 3 (a) N. Petragnani, R. Rodrigues and J. V. Cossemato, J. Organomet. Chem., 1976, 114, 281; (b) J. V. Comasseto, J. Organomet. Chem., 1983, 253, 131.
- 4 (a) J. V. Cossemato and N. Petragnani, J. Organomet. Chem., 1978, 152, 295; (b) N. Petragnani and J. V. Cossemato, Proceedings, XVIIIth International Conference on Coordination Chemistry, Brasil, 1977, p. 35.
- 5 Y. Z. Huang and Y. C. Shen, Adv. Organomet. Chem., 1982, 20, 115.
- 6 A. Toshimitsu, S. Umura and M. Okano, J. Chem. Soc., Chem. Commun., 1982, 87.
- 7 H. J. Reich, W. W. Willis and P. D. Clark, J. Org. Chem., 1981, 46, 2775.
- 8 (a) Q. G. Zhen, W. Y. Fu, B. C. Chen and X. Huang, Youji Huaxue, 1988, 8, 61; (b) Y. Z. Huang, L. L. Shi, S. W. Li and R. Huang, Synth. Commun., 1989, 19, 2639.

Paper 4/06532H Received 25th October 1994 Accepted 9th November 1994