

Synthesis of Acyl(phenylselanyl)methylidene(triphenyl)- λ^5 -arsanes and their Wittig-type Reactions

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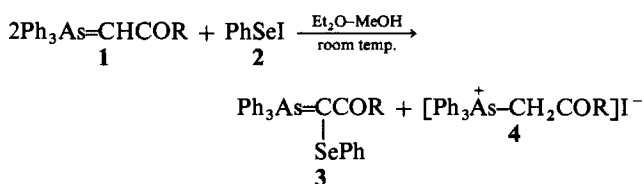
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Acyl(phenylselanyl)methylidene(triphenyl)- λ^5 -arsanes **3** have been synthesized by treating acylmethylidene(triphenyl)- λ^5 -arsanes **1** with phenylselanyl iodide **2**; α -selanylarsonium ylides **3** are sufficiently reactive to undergo Wittig-type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

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

To date there is no literature on the synthesis of α -selanylarsonium ylides. As arsonium ylides are strong nucleophiles and phenylselanyl halides are good electrophiles, we treated acylmethylidene(triphenyl)- λ^5 -arsanes **1** with phenylselanyl halides and found that a transylation reaction took place. Of the phenylselanyl halides tested, phenylselanyl chloride, phenylselanyl bromide and 'phenylselanyl iodide' prepared *in situ*,⁶ the last was the most reactive. Thus, in diethyl ether–methanol, acylmethylidene(triphenyl)- λ^5 -arsanes **1** (2 equiv.) react with phenylselanyl iodide **2** smoothly to produce acyl(phenylselanyl)methylidene(triphenyl)- λ^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 transylation reaction. The white crystalline acetyl(phenylselanyl)methylidene(triphenyl)- λ^5 -arsane **3a** decomposes at 180 °C and benzoyl(phenylselanyl)methylidene(triphenyl)- λ^5 -arsane **3b** has a melting point of 198–200 °C. Although acyl(phenylselanyl)methylidene(triphenyl)- λ^5 -arsanes **3** are sensitive to heat, light and moisture, it is possible to store them for use in subsequent reactions.



As expected, the acyl(phenylselanyl)methylidene(triphenyl)- λ^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 α,β -unsaturated aldehydes to produce α -

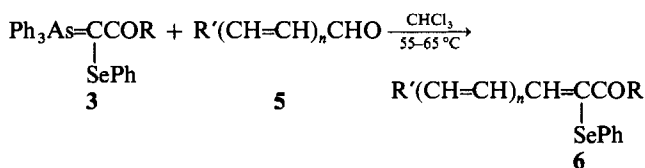
Table 1 Wittig-type reactions of α -selanylarsonium ylides **3**^a

Compound	R'	n	R	Yield (%)	Z: E ^b
6a	<i>m</i> -NO ₂ C ₆ H ₄	0	Me	80	90:10
6b	Ph	0	Me	75	75:25
6c	<i>p</i> -MeC ₆ H ₄	0	Me	65	70:30
6d	Ph	1	Me	81	91:9
6e	Me	1	Me	76	90:10
6f	Bu ^t	0	Me	61	80:20
6g	<i>p</i> -NO ₂ C ₆ H ₄	0	Ph	80	85:15
6h	Ph	1	Ph	81	92:8
6i	Bu ^t	0	Ph	70	85:15
6j	Me	1	Ph	72	91:9

^a The structures of all compounds were confirmed by ¹H NMR, IR, and mass spectroscopy and elemental analysis. ^b The ratio of *Z*- to *E*-isomer was estimated by ¹H NMR spectroscopy or GC.

phenylselanyl α,β -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.⁷ 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*)- α -selanyl α,β -unsaturated ketones **6**. The stereochemistry of this reaction is analogous to that observed in the Wittig-type reactions of α -iodoarsonium ylides.⁸

Research on other α -organoselanylarsonium ylides is now in progress.



Experimental

General Procedure for the Synthesis of Acetyl(phenylselanyl)methylidene(triphenyl)- λ^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 Et₂O–MeOH (5 cm³, 15:1 v/v), under nitrogen was added dropwise to a stirred suspension of acetylmethylidene(triphenyl)- λ^5 -arsane **1a** (0.724 g, 2 mmol) in Et₂O–MeOH (3 cm³, 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 cm³) was added to it. After filtration the residue was washed with diethyl ether (10 cm³ × 2) and then extracted with warm benzene (10 cm³ × 3). Filtration gave a powdery residue, which

was washed with tetrahydrofuran (THF) ($10 \text{ cm}^3 \times 2$) 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, δ_{H} 7.85–7.05 (m, 20 H) and 2.34 (s, 3 H); m/e 518 (M, 5.88%) and 78 (100.00); $\nu \text{ cm}^{-1}$, 1570s, 1500vs, 745vs and 685s (Found: C, 62.1; H, 4.5. Calc. for $\text{C}_{27}\text{H}_{23}\text{AsOSe}$: 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)- λ^5 -arsane **3a** (0.776 g, 1.5 mmol) and benzaldehyde **5b** (0.106 g, 1 mmol) in chloroform (3 cm^3) in the dark was stirred at 55–65 °C for 7 days under a N_2 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%); δ_{H} 7.97 (s, 0.75 H, Z-4-H), 7.85–6.70 (m, 10.25 H, 2 of C_6H_5 + E-4-H), 2.34 (s, 0.75 H, Z- CH_3) and 2.07 (s, 0.25 H, Z- CH_3); m/z 302 (M, 22.62%) and 43 (100.00); $\nu \text{ cm}^{-1}$ 1675vs, 1605s, 734vs and 685s (Found: C, 63.8; H, 4.7. Calc. for $\text{C}_{16}\text{H}_{14}\text{OSe}$: C, 63.79; H, 4.68).

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