

A Convenient Synthesis of α -Phenylseleno- α , β -unsaturated Nitriles *via* Arsonium Salt

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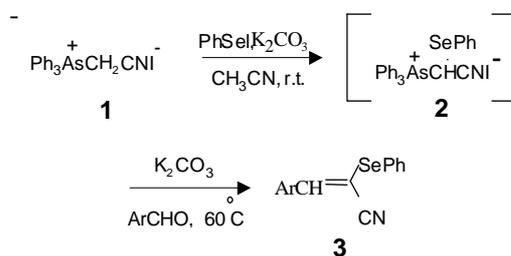
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Abstract: α -Phenylseleno- α , β -unsaturated nitriles were synthesized under mild condition *via* arsonium salt **1** in one pot reaction.

Keywords: Unsaturated nitriles, phenylselenenylation, synthesis, arsonium salt.

α -Phenylseleno- α , β -unsaturated nitriles are useful intermediates in organic synthesis in consequence of the considerable versatility of the transformation of seleno^{1,2} and cyano, good dienophiles and radicophiles³. However, only one method for their preparation have been reported,⁴ but its yield is very low. Recently, our interest in synthesis and application of α -seleno arsonium ylides led us to exploit α -selenenylation of arsonium salt **1** and consequent condensation with aromatic aldehydes under weakly basic condition. Herein we wish to report an efficient one pot synthesis of α -phenylseleno- α , β -unsaturated nitriles *via* the easily available arsonium salt **1**.

The arsonium salt **1** was prepared by triphenylarsine and chloroacetonitrile in the presence of potassium iodide under reflux. Compound **1** is a light yellow crystals, m.p. 155-156 °C, yield 81%.



The arsonium salt **1** reacted with phenylselenenyl iodide in the presence of anhydrous potassium carbonate in acetonitrile at room temperature to produce the α -seleno arsonium iodide **2** which, without isolation, was reacted with aromatic aldehydes to afford α -phenylseleno- α , β -unsaturated nitriles **3** in good yields as listed in **Table 1**.

Table 1. The Preparation of α -Phenylseleno- α,β -Unsaturated Nitriles

Entry ^a	Ar	Reaction time(hr.) ^b	m.p. (°C)	Isolated Yield (%)
3a	<i>p</i> -CH ₃ OC ₆ H ₄	26	80-82 ^c	70
3b	<i>p</i> -O ₂ NC ₆ H ₄	24 ^d	196-198 ^e	85
3c	<i>o</i> -O ₂ NC ₆ H ₄	14	62-64 ^c	86
3d	<i>m</i> -O ₂ NC ₆ H ₄	26	65-67 ^c	80
3e	<i>p</i> -ClC ₆ H ₄	24 ^d	57-60 ^e	78
3f	<i>p</i> -BrC ₆ H ₄	21	49-51 ^c	70
3g	<i>o</i> , <i>p</i> -Cl ₂ C ₆ H ₃	22	52-53 ^c	75

a) All compounds were confirmed by ¹H NMR, IR, MS and elemental analysis.

b) The phenylselenenylation of arsonium iodide **1** was completed after 8 h.

c) crystallized from diethyl ether.

d) Reaction temperature: room temperature.

e) crystallized from CCl₄.

Preparation of 3-(4-Methoxyphenyl)-2-phenylselenoacrylonitrile **3a**. A mixture of triphenylcyanomethylenearsonium iodide **1** (0.473 g, 1.0 mmol), potassium carbonate (0.138 g, 1.0 mmol) and phenylselenenyl iodide (1 mmol) in acetonitrile (4 ml) was stirred at room temperature under nitrogen. After 8 h, the color of phenylselenenyl iodide almost disappeared, indicating that the reaction was completed. *p*-Methoxybenzaldehyde (0.11 g, 0.9 mmol), potassium carbonate (0.138 g, 1 mmol) and a trace water (10 μ l) were added into the above mixture. After stirring at 60 °C (oil-bath) for 26 h, the reaction was completed (monitored by TLC). After cooling, diethyl ether (10 ml) was added to the reaction mixture and then filtered to remove triphenylarsine oxide and inorganic salts. The filtrate was concentrated and separated on a preparative TLC (light petroleum-diethyl ether 7:3 as eluent) to afford **3a**. ¹H NMR (60MHz, CCl₄, HMDS): δ ppm 7.69 (d, 2H, J=9Hz), 7.55-7.22 (m, 6H, aromatic and vinyl hydrogen), 6.84 (d, 2H, J=9Hz), 3.74 (s, 3H); MS (m/z): 314 (M⁺, 35.97), M+1, M+2, M+3, 299, 283, 235 (100%), 220, 204, 197, 157, 116, 77, 51; IR (KBr) cm⁻¹ 2200(m), 1610(s), 1510(s), 1425(m), 1315(m), 1260(s), 1180(s), 1125(m), 825(m), 735(s); Anal. (calcd. for C₁₆H₁₃N₂OSe): C, 61.17; H, 4.17; N, 4.46. Found: C, 61.15; H, 4.23; N, 4.39).

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