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A simple one-pot synthesis of phosphinoselenoic amides and diamides from secondary phosphine selenides and amines using Et₃N-CCl₄

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ABSTRACT

The multi-component reaction between secondary phosphine selenides and amines (primary, secondary, and primary diamines) proceeds using the Et₃N-CCl₄ system under mild conditions to give phosphinose-lenoic amides or diamides in 81–89% isolated yields.

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Phosphinic and phosphinothioic amides and diamides are employed extensively as ligands for the design of metal-complexes,¹ precursors of biologically active drugs² and building blocks in organic and elementoorganic synthesis.³ Phosphinoselenoic amides and diamides also attract continued research interest. For example, complexes of these phosphinoselenoic amides with transition metals (Ti, Cr, Mn, Fe, Co, Ni, Zn, Cd)⁴ are successfully used as singlesource precursors for the preparation of metal selenide thin films.^{4c,d} Diphenylphosphinoselenoic amides are known to be acetylcholinesterase inhibitors.⁵ However, the conventional syntheses of phosphinoselenoic amides are tedious and involve utilizing moisture- and air-sensitive phosphorus halides^{4a,5,6} and, in some cases, difficult to obtain organylamides of alkali metals.^{4a,6c-f} The Todd-Atherton reaction, which was discovered and investigated using dialkyl phosphites,⁷ and briefly described for secondary phosphine oxides and phosphine sulfides,⁸ represents a simple and convenient approach to phosphinoselenoic amides. Reports on the possible application of secondary phosphine selenides in Todd-Atherton type reactions are absent in the literature.

In this paper, we report for the first time the multi-component one-pot reaction of secondary phosphine selenides with primary and secondary amines and primary diamines using the Et₃N-CCl₄ system.

Experiments have shown⁹ that secondary phosphine selenides **1** and **2** react with primary **3** and **4**, or secondary amines **5–7** using the Et₃N-CCl₄ system under mild conditions (20–25 °C, 1 h) to afford diphenyl- and bis(2-phenylethyl)phosphinoselenoic amides **8a–f** in 82–87% isolated yields (Table 1).

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The mechanism of this reaction can be rationalized as follows (Scheme 1). P.Se-ambident selenophosphinite anion A. formed via deprotonation of the secondary phosphine selenide 1 or 2 under the action of triethylamine, reacts with carbon tetrachloride to furnish phosphinoselenoic chloride **B** and the ⁻CCl₃ carbanion. Protonation of the latter by a triethylammonium cation leads to regeneration of triethylamine and formation of chloroform. Phosphinoselenoic chloride **B** reacts with the primary or secondary amine 3-7 in the presence of triethylamine to give phosphinoselenoic amides 8a-f and triethylammonium chloride. Bis(2-phenethyl)phosphinoselenoic chloride¹⁰ and chloroform were identified in the reaction mixture by ¹H, ¹³C and ³¹P NMR spectroscopy.

The reaction was found to be general in character. Secondary phosphine selenides possessing aryl and arylalkyl substituents, as well as different primary and secondary amines, including unsaturated examples, participated readily in this multi-component reaction. The general character of the reaction is additionally supported by the fact that diamines can also be employed in this reaction.

For example, primary diamines **9–12** react readily (20–25 °C, 1 h) with two equivalents of the secondary phosphine selenides **1** or **2** in Et₃N-CCl₄ to furnish the corresponding diamides **13a–e** in 81–89% yield¹¹ (Table 2).

In summary, the multi-component reaction between secondary phosphine selenides and various amines or diamines using the Et₃N-CCl₄ system affords phosphinoselenoic amides and diamides in high yields. The polyfunctional compounds synthesized are prospective ligands for the preparation of metal-complexes, promising intermediates for the production of conducting nanomaterials, precursors for the design of biologically active compounds, and building blocks for elementoorganic synthesis.



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Table 1

Synthesis of phosphinoselenoic amides 8a-f^a



		, .	-1					
Entry	R ¹ ₂ P(Se)H 1 , 2 (1 mmol)	R ¹	R ² R ³ NH 3–7 (1 mmol)	R ²	R ³	Product	Yield (%)	
							b	с
1	1		6	<i>n</i> -Pr	<i>n</i> -Pr	8a	90	82
2	2		3	Н	Allyl	8b	89	83
3	2		4	Н	Ph	8c	94	86
4	2		5	Et	Et	8d	91	83
5	2		6	<i>n</i> -Pr	<i>n</i> -Pr	8e	93	87
6	2		7	n-Bu	<i>n-</i> Bu	8f	90	82

^a All experiments were carried out under argon at r.t. for 1 h; Et₃N (1 mmol) and CCl₄ (4 ml) were used.

^b Yields calculated from the ³¹P NMR spectra of the crude products.

^c Isolated yield.





Table 2

Reaction of phosphine selenides 1 and 2 with diamines 9-12^a

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A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.02.095.



^a All experiments were carried out under argon at r.t. for 1 h; Et₃N (1 mmol) and CCl₄ (4 ml) were used.

^b Yields calculated from the ³¹P NMR spectra of the crude products.

^c Isolated yield.

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- 9. General procedure for the synthesis of phosphinoselenoic amides **8a–f**. A mixture of secondary phosphine selenide **1** or **2** (1.0 mmol) and Et₃N (101 mg, 1.0 mmol) in CCl₄ (4 ml) was stirred at 20–25 °C for 10 min. A solution of amine **3–7** (1.0 mmol) in CCl₄ (1 ml) was added, and the mixture was stirred at 20–25 °C for 50 min. The solvent was removed under reduced pressure, and 1,4-dioxane (3 ml) was added. The precipitated white solid (triethylammonium chloride) was removed by filtration and the 1,4-dioxane evaporated under vacuum. The residue obtained was washed with hot hexane (2 × 3 ml), and the hexane solution was allowed to stand for 12 h at 0–1 °C. The hexane layer was filtered and evaporated under vacuum. The residue was dried in vacuo to give amides **8a–f**.
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- 11. General procedure for the synthesis of phosphinoselenoic diamides **13a–e**. A mixture of secondary phosphine selenide **1** or **2** (1.0 mmol) and Et₃N (101 mg, 1.0 mmol) in CCl₄ (4 ml) was stirred at 20–25 °C for 10 min. A solution of diamine **9–12** (0.5 mmol) in CCl₄ (1 ml) was added, and the reaction mixture stirred at 20–25 °C for 50 min. The solvent was removed under reduced pressure, and 1,4-dioxane (3 ml) was added. The precipitated white solid (triethylammonium chloride) was removed by filtration and the 1,4-dioxane (3 × 2 ml), and the hexane was removed by decanting. The residue was dried under vacuo to give diamides **13a–e**.