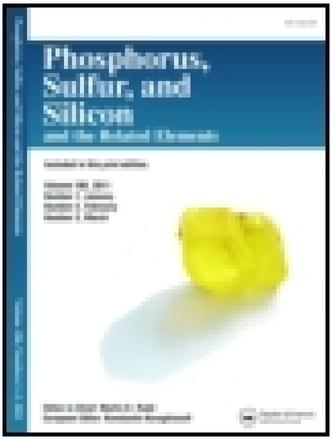

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A Convenient Synthesis of Phenyl 1-Chloro-1 Alkenyl Chalcogenides by One-Pot Wittig Reaction. Synthesis of Selenolesters

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The preparation of 1-chloro-1-chalcogeno(sulfur, selenium) alkenes by a Wittig-type reaction in an one pot procedure is described. Chlorochalcogenyl triphenylphosphoranes are formed *in situ* by the reaction of dichloromethyl phenylchalcogenide, potassium *t*-butoxide and triphenylphosphine. They react with aldehydes to give 1-chlorovinyl chalcogenides as a mixture of isomers.

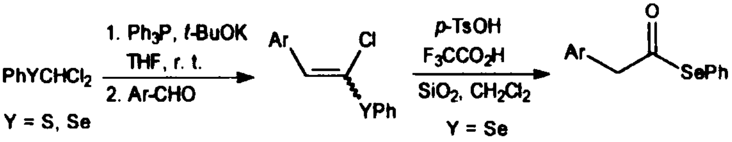
Keywords: Wittig reaction; vinylic sulfides; vinylic selenides; vinyl halides

INTRODUCTION

Vinylic chalcogenides constitute a very useful class of compounds due to their versatility in organic synthesis.[1] The substituted α-halo-α-chalcogen olefins have attracted considerable interest in recent years and a few methods were described for their preparation such as the treatment of 1-(phenylthio)-vinylstannanes with copper (II) halides,[2] by addition of HX (X = Cl, Br, I) chalcogen acetylenes,[3] by the reaction of 1-tosylvinyl selenides with MgX_2,[4] through Wittig-Horner-type reactions[5] and by means of phase transfer conditions.[6]

RESULTS AND DISCUSSION

Recently we described a convenient synthesis of vinyl sulfides, selenides and tellurides based on a very convenient one-pot procedure,[7] consisting of the addition of potassium *t*-butoxide to a solution of chloromethylchalcogenide and triphenylphosphine in THF followed by addition of an aldehyde or a ketone. Herein we describe that this method can also be conveniently applied to the synthesis of chlorovinyl phenylsulfides[8] and phenylselenides (1-chloro-1-chalcogeno alkenes). In this way, treatment of a THF solution of 1,1-dichloro-1-chalcogenomethane[9] **1-2** with *t*-BuOK, Ph_3P and an aldehyde at room temperature, furnishes the desired products in moderate to good yields, after usual work-up and purification by column chromatography on silica gel (Scheme 1, Table 1). The total reaction sequence **1-2** to **3-4** is achieved in one pot, without isolation of the intermediate chalcogeno phosphoranes. We believe that the formation of **3-4** is in accordance with the mechanism previously proposed for the preparation of vinylic chalcogenides[7] in which the first step probably involves an α-elimination of HCl from **1-2** by the action of *t*-BuOK, forming transiently the corresponding α-chlorochalcogenocarbenes which are trapped by triphenylphosphine leading to the chlorochalcogeno phosphoranes that promptly react with an appropriate aldehyde.



SCHEME 1

1-Halo-1-chalcogenoalkenes are poorly investigated compounds and little is known about their reactivity. Recently few transformations with this class of compounds were reported, such as the conversion of 1-chloro-1-selenoalkenes into the corresponding 1-metalated derivatives followed by the reaction with electrophiles,[3] the hydrolysis of 1-chloro-1-phenylthioalkenes to thiolesters,[10] the Pd-catalysed cross-coupling reaction with alkynes[11] and their Friedel-Crafts-type reaction to give 1-arylalkenyl sulfides.[2] In order to illustrate the usefulness of the less studied selenium compounds, we performed the hydrolysis of the 1-chloro-1-phenylseleno alkenes into the corresponding selenolesters, in accordance with Scheme 1. Therefore, chlorovinyl selenides **4a**, **4d** and **4e** were hydrolyzed to **5a**, **5d** and **5e** respectively, by the treatment with a mixture of trifluoracetic acid and p-toluenesulfonic acid in dichloromethane, adding to it a small amount of silica gel. Under these conditions, the selenolesters were obtained in an non-optimized yield of ca. *50%*. We have observed that the use of a mixture of both acids was crucial to the success of the method. This reaction constitutes one of the few possibilities to prepare selenolesters/thiolesters from a methodology involving a C-C bond formation. The other methods available make use of alkynes or other carbonylic derivative as starting materiais.

These olefination reactions give rise to an isomeric *Z*/*E*-mixture, with low stereoselectivity (1.5:1 to 5:1 ratio). The *Z*-isomer was detected as the major component in the mixture, in accordance with the known stereochemical course of the Wittig olefinations under lithium salt free conditions.[12] In summary, the above methods provide ready access to α-chlorovinyl suifides and selenides, and to selenolesters, compounds of great interest as potential synthetic intermediates. It is worth mentioning the fact that the corresponding sulfides can also be transformed into α-chlorovinyl sulfoxides and sulfones by oxidative procedures.

TABLE 1. 1-Chloro-1-chalcogenoalkenes prepared from 1,1-dichloro-1-Chalcogenomethane.

Product[a]	Ar	Time (h)	Yield[b] (%)
3a	Phenyl	0,5	65
3b	2-furyl	0,5	77
3c	4-nitrophenyl	0,6	67
3d	4-methylphenyl	0,6	60
3e	4-chlorophenyl	0,6	60
4a	Phenyl	0,5	50
4b	2-furyl	0,5	63
4c	4-nitrophenyl	0,6	58
4d	4-methylphenyl	0,6	53
4e	4-chlorophenyl	0,6	51

a) All new compounds were fully characterized by ^{1}H-, ^{13}C-NMR, IR, MS and elemental analyses; b) Isolated yields;

EXPERIMENTAL

Typical Procedure for Chlorovinyl Selenide 4a: To a round botomed flask containing a solution of $PhSeCHCl_2$ (0.24g, 1.0 mmol) and Ph_3P (0.26g, 1 mmol) in dry THF (4 mL), under nitrogen, was added in portions *t*-BuOK (0.22g, 2.0 mmol). The reaction mixture became redish and after 5 min PhCHO (1.5 mmol) was added. The reaction mixture was stirred at r. t. for 30 min, quenched with water (50 mL) and extracted with ethyl acetate (2 x 20 mL), dried ($MgSO_4$), filtered and the solvent removed. The residue was purified by column chromatography on silica gel (eluent hexane) to give **4a**, 146 mg (50%).

^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.25-8.10 (m, 11H); IR (film): 1576 cm^{-1}; *m/z* (GC/MS): 294 (100%, M^+.), 257, 173, 102.

Hydrolysis to 5a: In a 25 mL flask, under argon, 4a (1 mmol) was dissolved in dichloromethane (5 mL). To this solution was added silica gel (0.5 g), p-TsOH (0.17g, 1 mmol) and CF_3CO_2H (0.11 g, 1 mmol) and the mixture was maintained under a gentle reflux for 48 h, cooled to room temperature, dissolved in dichloromethane, washed with water, dried ($MgSO_4$), and then the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel to give 144 mg (52%) **5a**, m.p.: 39-40 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ = 3.91 (s, 2H); 7.28-7.50 (m, 10H); ^{13}C (50 MHz, $CDCl_3$) 53.5; 126.6; 127.7; 128.7: 128.8. 129.0; 129.2;130.0; 132.5; 198.6; IR (film): 1709.5 *cm*$^{-1}$; *m/z* (GC/MS): 276 (2%, M^+), 157(5%); 119 (18%); 91 (100%); Anal. Calcd for $C_{14}H_{12}OSe$ (276.00): C, 61.10; H, 4.39. Found: C, 61.25; H, 4.48.

ACKNOWLEDGMENTS

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[12] For a discussion on this matter see C.C. Silveira, G. Perin, A.L. Braga and N. Petragnani, *Synlett*, 58 (1995).