



Regiospecific Hydroselenation of Terminal Acetylenes using Aluminum Phenylselenolate Anions

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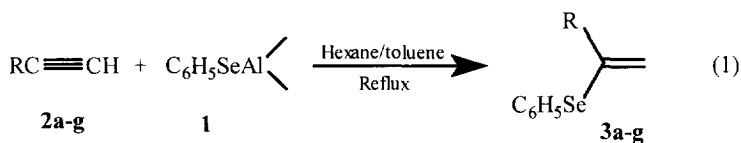
Abstract. Regiospecific hydroselenation of terminal acetylenes using aluminum phenylselenolates afforded the 1-organyl-1-phenylseleno ethenes in good yields. The first example of exclusive formation of the hydroselenation Markovnikov adducts is described. Copyright © 1996 Elsevier Science Ltd

Vinyl selenides are important reagents and intermediates in organic synthesis.¹ Despite the plethora of procedures for the synthesis of vinyl selenides there is a relative paucity of a general synthetic methodology for obtaining the 1,1-disubstituted isomers.^{1,2} Free-radical addition of phenyl selenol to terminal acetylenes at 50 °C preferentially provides the anti-Markovnikov products of *Z* configuration,³⁻⁷ but at 120 °C a mixture of *Z* and *E* vinyl selenides is formed.⁷ Two papers report on the synthesis of 1-phenylseleno-1-alkyl ethenes from the corresponding olefins *via* the addition of phenylselenenyl halides under kinetic control, followed by dehydrohalogenation of the β-haloalkyl phenyl selenides.^{8,9} In a more recent paper the use of transition-metal-catalyzed hydroselenation of acetylenes was described by Japanese authors.² They observed the formation of a mixture of products with several transition metal catalysts, including Pd(OAc)₂. However using the last catalyst the 1-alkyl-1-phenylseleno ethenes were obtained as the major products (with high selectivity) among the 1,2-disubstituted isomers when alkyl groups were linked at the triple bond of the starting material. In the case of phenyl acetylene a mixture containing 64% of the 1,2-disubstituted isomer (mixture of *Z* and *E* isomers) and 33% of the 1,1-disubstituted isomer was formed.

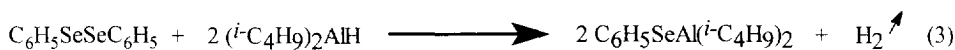
These facts and our interest in the chemistry of vinyl chalcogenides prompted us to investigate methodologies of general scope to transform terminal acetylenes exclusively into the 1-phenylseleno-1-organyl ethenes and we report here our results on the synthesis of these compounds by the regiospecific hydroselenation of terminal acetylenes using aluminum phenylselenolate anions.

In the methodology developed by us, the aluminum phenylselenolates **1** were added to a terminal acetylene under reflux for 24 hours and the only olefinic products formed are depicted in

equation 1. The methodology was applied to acetylenes **2a-g** containing alkyl (entries 2 and 3), aryl (entry 1), and hydroxyl groups (entries 4-7). In all cases the only olefinic products detected by the analytical methods employed (^1H NMR, CG/MS, ^{13}C NMR) were the 1,1-disubstituted isomers **3a-g**. These products were formed in moderate to good yields as shown in Table 1.



The aluminum phenylselenolates were generated and used *in situ* by the reaction of diphenyl diselenide with DIBAL-H or $(\text{C}_2\text{H}_5)_3\text{Al}$. It is important to note that best results were obtained using the aluminum phenylselenolate anion generated by reaction with DIBAL-H (Table 1). In the case of reaction with $(\text{C}_2\text{H}_5)_3\text{Al}$ one equivalent (at least) of $\text{C}_6\text{H}_5\text{SeC}_2\text{H}_5$ was formed as a side product (Eq. 2), while in the reaction with DIBAL-H theoretically two equivalents of the selenolate anion must be formed (Eq. 3).^{10,11} However, under the conditions used here formation of some $\text{C}_6\text{H}_5\text{Se}^i\text{-C}_4\text{H}_9$ was observed,¹² reducing the yield of the selenolate formation. Similar result was observed by us when we obtained $\text{C}_4\text{H}_9\text{TeAl}(^i\text{-C}_4\text{H}_9)_2$ from dibutyl ditelluride and DIBAL-H.¹³



In a previous paper¹³ we reported that three equivalents of acetylene are necessary for a complete reaction when the aluminum butyltellurolate anion is used since the acetylene acts as a proton source to protonate the vinylaluminum intermediate. However, capturing this intermediate with electrophiles was not possible.¹³ In the reaction described here with the corresponding phenyl selenolate, three equivalents of acetylene were also used.¹⁴ Reaction of phenyl acetylene results in the formation of a mixture of the (*Z*)-1,2-disubstituted and the 1,1-disubstituted isomers in a 25:75 ratio, when phenylacetylene is added to the solution containing the recently prepared mixture of $\text{C}_6\text{H}_5\text{Se}$ ⁻ and DIBAL-H (after 5 min) followed by reflux. However, refluxing the solution of $\text{C}_6\text{H}_5\text{SeAl}(^i\text{-C}_4\text{H}_9)_2$ for 2 hours prior to the addition of phenylacetylene and stirring the reaction under reflux for an additional 24 hours only the 1,1-disubstituted isomer **3a** was obtained in 85% yield (entry 1, Table 1). For all other examples only the 1,1-disubstituted isomers were formed and the 1,2-disubstituted isomer was never detected under any of the conditions employed. It is of fundamental importance to

use recently distilled solvents and alkynes since attempts to avoid this procedure result in very poor yields and no reaction in some cases.

Table 1. 1-Phenylseleno-1-organyl ethenes obtained by using $C_4H_9SeAl(C_4H_9)_2$.

Entry	Acetylene	Product ^a	Yield (%) ^{b,c}
1	$C_6H_5C\equiv CH$ 2a		85
2	$C_6H_{13}C\equiv CH$ 2b		68
3	$C_4H_9C\equiv CH$ 2c		72
4	 2d		56
5	 2e		45
6	 2f		55
7	 2g		53

^aSpectral data are in accordance with the proposed structures. ^bIsolated yields. ^cPurified by flash chromatography.

In entries 4-7 (Table 1), triethyl aluminum was used to protect *in situ* the free hydroxyl group present in the acetylenic compounds^{15,16} and the resulting colorless solution was later added to the aluminum phenylselenolate. However, yields were moderate because the alkyl phenyl selenides were formed in increasing amounts.

The following experimental procedure is representative of this conversion: To a yellow solution of diphenyl diselenide (0.936g; 3.0mmol) in anhydrous hexane (10 mL) under dry nitrogen at room temperature a solution of DIBAL-H in toluene (6.0 mmol; 6.0 mL; 1.0 M) was added. Upon completion of the addition, the colorless solution was stirred at this temperature for two hours. Then, the appropriate acetylene (18.0 mmol) was added¹⁶ and the solution stirred at reflux for 24 hours. The solution was then cooled at 0 °C and water (20 mL) was slowly added under nitrogen and stirring

was continued for an additional 10 min. The product was extracted with a mixture of hexane/ethyl acetate (8/2) and washed with a saturated NH_4Cl solution. After drying the organic phase over anhydrous MgSO_4 , the solvents were removed under reduced pressure. The products were purified by flash chromatography using hexane (for entries 1-3; Table 1) or a mixture of hexane/EtOAc (8/2) (for entries 4-7; Table 1). Yields are shown in Table 1.

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