STEREOSELECTIVE SYNTHESIS OF VINYLIC SELENIDES

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Abstract

The addition of selenophenol to mono- and di-substituted unactivated acetylenes have been investigated. At room temperature the vinylic selenides obtained were predominantly of the Z configuration; at 120°C Z/E mixtures were produced. Vinylic selenides with the E configuration were obtained by reduction of the corresponding selenoacetylenes with lithium aluminium hydride.

Introduction

In recent years, several methods for the preparation of vinylic selenides have been reported [1—12]. A simple route to these intermediates would be the addition of a selenophenol to an acetylene. However, this reaction has received little study and most of the work in this area has dealt with the addition of selenophenol to activated acetylenes, i.e., "Michael-type" additions [13—24]. According to the few available reports, the addition of selenophenol to phenylacetylene and 1-hexyne gives the Z isomer as the main product [13—18] and the addition to 1-hexyne was claimed to occur only on prolonged heating in the presence of a basic catalyst [17]. In the course of work directed towards the stereoselective synthesis of vinylic selenides we have studied the reaction of selenophenol with some mono- and di-substituted unactivated acetylenes [2a,25]. The increasing interest in this type of intermediate [3,4,8—11,26,27] prompted us to extend this work. We have carried out the reaction of selenophenol with eight acetylenes in the absence of a basic catalyst at various temperatures.

$$RC{\equiv}CR' \xrightarrow{\text{PhSeH}} RCH{=}CR'SePh$$
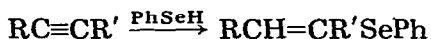
R = Ph, R' = H; R = Ph, R' = CH₃; R = Ph, R' = C₂H₅; R = Ph, R' = n-C₃H₇; R = Ph, R' = n-C₄H₉; R = n-C₃H₇, R' = H; R = n-C₄H₉, R' = H; R = n-C₄H₉, R' = n-C₄H₉

On the other hand it is well known that acetylenes are reduced by LiAlH₄ (LAH) in refluxing THF, furnishing the olefin with E configuration [28]. This suggested the use of the readily available selenoacetylenes as starting materials to prepare vinylic selenides with the E configuration. We have carried out the reduction of three selenoacetylenes by this method:
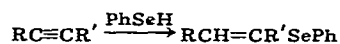
$$RC≡CH \xrightarrow[\text{2) PhSeBr}]{\text{1) n-BuLi}} RC≡CSePh \xrightarrow{\text{LAH}} RCH=CHSePh$$

$R = Ph, n-C_3H_7; n-C_4H_9$

Results and discussion

The addition of selenophenol to acetylenes was performed simply by heating equimolar amounts of the reagents in a sealed tube. After the reaction times indicated in Table 1, the reaction mixture was immediately worked up and analysed by ¹H NMR and IR spectroscopy and by GLC.

In the case of phenylacetylene the reaction was immediate and exothermic and gave predominantly the Z isomer, as previously reported [2a]. The addition of aryl- and alkyl-disubstituted acetylenes, as well as to monosubstituted alkyl-acetylenes, in contrast to previous claims [17], occurred even at room temperature in the absence of a basic catalyst. The reaction is slow at room temperature and requires long reaction time. The rate becomes faster at higher temperatures. When the reaction is performed at room temperature, the vinylic selenides which result exhibit predominantly the Z configuration, the yields decreasing with increase in chain length of R′. The stereoselectivity was observed to be temperature dependent. At 50°C, the amount of E olefin is increased, althoug' the olefin with Z configuration is still predominant. At 120°C, the stereoselectivity is lost, and approximately equal amounts of the Z and E vinylic selenide are formed. At the higher temperatures (120°C), the formation of some by-products in minor amounts was observed in the reactions with 1-pentyne and 1-hexyne, but it was not possible to separate and identify them.

TABLE 1

$$RC≡CR' \xrightarrow{\text{PhSeH}} RCH=CR'SePh$$

	R	R'	Yield (%) [a], Z/E ratio [b]		
			r.t./240 h	50°C/48 h	120°C/24 h
I	Ph	H	90 [c] > 95Z	—	—
II	Ph	CH₃	90 > 95Z	85 35/65 [d]	64 40/60 [d]
III	Ph	C₂H₅	80 > 95Z	80 > 95Z	65 [e] 70/30
IV	Ph	n-C₃H₇	45 > 95Z	76 > 95Z	69 [e] 60/40
V	Ph	n-C₄H₉	45 > 95Z	74 > 95Z	76 [e] 50/50 [d]
VI	n-C₃H₇	H	44 > 95Z	46 > 95Z	64 [f] 50/50
VII	n-C₄H₉	H	45 > 95Z	42 > 95Z	69 [f] 50/50
VIII	n-C₄H₉	n-C₄H₉	trace	trace	45 50/50

[a] Yield after column chromatography purification. [b] Determined by GLC, unless otherwise indicated. [c] The reaction is completed in few minutes at room temperature. [d] Determined by ¹H NMR spectroscopy. [e] Yield of the "normal" and rearranged (compounds IX, X and XI) addition products. [f] Chromatographic purity: ~95%.

The configurations of the E and Z isomers were assigned based on NMR, and IR data in the case of the disubstituted olefins (see Tables 2 and 4), and by chromatographic comparison with the product of a Horner reaction assumed to be the E isomer (see ref. 2b), in the case of trisubstituted olefins.

The stereochemistry of the addition at the lower temperatures can be understood on the basis of the mechanisms already proposed [16—18]:

a) Nucleophilic attack of selenophenol at the triple bond, leading to the more stabilized carbanion in the case of arylacetylenes. In the case of alkylacetylenes, the attack is controlled by steric factors, occurring at the less hindered site. In both cases, the PhSe group and the electron pair of the intermediate are in *anti* orientation. Protonation of the intermediate furnishes the vinylic selenide with Z configuration.

$$PhSeH \rightleftharpoons PhSe^- + H^+$$
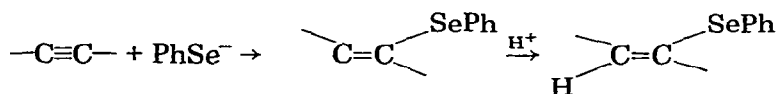
b) Participation of two moles of PhSeH in an *anti* fashion as depicted below:
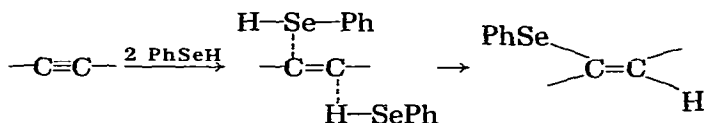
The formation of a mixture of isomers in the reaction occurring at $120°C$ could be explained in terms of an isomerization of the initially formed Z isomer. This supposition is supported by the observed isomerization of the pure Z isomer (entries VI and VII) upon heating for several hours in a sealed tube.

On the other hand, the trimolecular mechanism proposed by Russian authors [18] could also be responsible for the E configuration of the product obtained at high temperature.
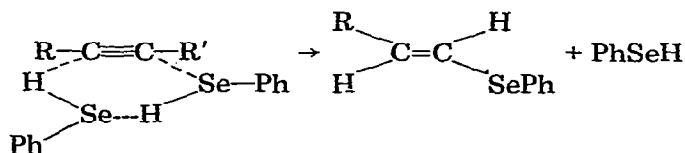
An unexpected result was observed with substituted aromatic acetylenes ($R > CH_3$) in reactions at $120°C$. In addition to the "normal" addition products to the triple bond of 1-phenyl-1-butyne, 1-phenyl-1-pentyne and 1-phenyl-1-hexyne the compounds IX, X and XI, respectively, were obtained.
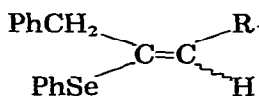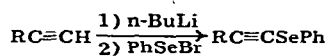

(IX, $R = CH_3$;
X, $R = C_2H_5$;
XI, $R = C_3H_7$)

TABLE 2

	Analyses Found (calcd.) (%)		^{1}H NMR data for the Z isomer (δ (ppm), J(Hz), TMS internal reference
	C	II	
I	[2a]		a) 6.76 (AB quartet, $J = 10$) [a] b) 7.0—7.6 (10 H, m)
II	[2a]		a) 2.03 (3 H, d, $J_{ab} = 1.5$) b) 6.73 (1 H, q, $J_{ba} = 1.5$) [b] c) 7.0—7.6 (10 H, m)
III	66.43 (66.92)	5.55 (5.57)	a) 1.16 (3 H, t, $J_{ab} = 7$) [b] b) 2.30 (2 H, dq, $J_{ba} = 7$, $J_{bc} \sim 1$) c) 6.80 (1 H, t, $J_{cb} \sim 1$) d) 7.1—7.6 (10 H, m)
IV	67.40 (67.77)	6.13 (5.98)	a) 0.83 (3 H, t, $J = 7$) [b] b) 1.0—1.8 (2 H, m) c) 1.23 (2 H, q, $J = 7$) d) 6.73 (s, 1 H) e) 7.0—7.6 (10 H, m)
V	68.26 (68.59)	5.88 (6.34)	a) 0.6—1.8 (7 H, m) [b] b) 2.43 (2 H, t, $J_{bc} \cong 7$) c) 6.78 (1 H, s) d) 7.0—7.6 (10 H, m)

Structures (left column):

I: H$_a$H C=C with Ph$_b$ and SePh$_b$

II: CH$_3{}^a$ / H$_c$ C=C with Ph$_c$ and SePh$_c$

III: CH$_2$CH$_3$ (b, a) / H$_c$ C=C with Ph$_d$ and SePh$_d$

IV: CH$_2$CH$_2$CH$_3$ (c, b, a) / H$_d$ C=C with Ph$_e$ and SePh$_e$

V: CH$_2$CH$_2$CH$_2$CH$_3$ (b, a) / H$_c$ C=C with Ph$_d$ and SePh$_d$

VI

CH$_3$CH$_2$CH$_2$ (a, b, c) — C=C — SePh (f), H (n)

58.40
(58.70)

6.50
(6.22)

a) 0.8–1.1 (3 H, m) [c]
b) 1.2–1.6 (2 H, m)
c) 1.9–2.3 (2 H, m)
d) 6.00 (1 H, dt, J_{de} = 9, J_{dc} = 7)
e) 6.40 (1 H, dt, J_{ed} = 9, J_{ec} = 1)
f) 7.0–7.6 (5 H, m)

VII

CH$_3$(CH$_2$)$_2$CH$_2$ (a, b, c) — C=C — SePh (f), H (e), H (d)

[4]

a) 0.8–1.1 (5 H, m) [c]
b) 1.2–1.6 (4 H, m)
c) 1.9–2.4 (2 H, m)
d) 6.01 (1 H, dt, J_{dc} = 7, J_{dc} = 9)
e) 6.41 (1 H, dt, J_{ed} = 9, J_{ec} ≃ 1)
f) 7.0–7.6 (5 H, m)

VIII

CH$_3$CH$_2$CH$_2$CH$_2$CH (a, b, c, d)=C(SePh)CH$_2$CH$_2$CH$_2$CH$_3$ (b, a)

64.95
(65.11)

7.82
(8.13)

a) 0.6–1.7 (14 H, m) [d]
b) 1.9–2.5 (4 H, m)
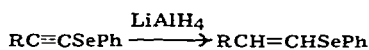c) 5.80 (1 H, t, J_{cb} = 7)
d) 7.0–7.6 (5 H, m)

[a] Spectra registered on a XL 100 spectrometer in CCl$_4$. The vinylic proton of PhCH=CDSePh resonates at δ 6.90 ppm. For IR data see ref. 2a. [b] Compared with the main product of a Horner-Emmons Reaction, assumed to be the E isomer [2b,25]. [c] The IR band at 950 cm^{-1} (out-of-plane deformation in the *trans* isomer) is completely absent. [d] Product of the reaction at room temperature.
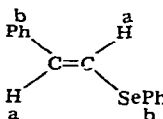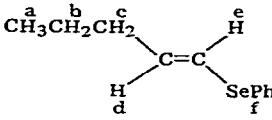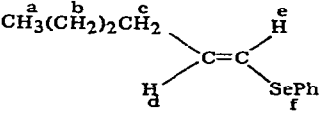
TABLE 3

$$RC{\equiv}CH \xrightarrow[\text{2) PhSeBr}]{\text{1) n-BuLi}} RC{\equiv}CSePh$$

	RC≡CHSePh	Yield (%)	Analyses Found (calcd.) (%)		^{1}H NMR data (δ(ppm), J(Hz), TMS internal reference)
			C	H	
XII	PhC≡CSePh	90	[2a]		[2a]
XIII	$\overset{a}{C}H_3\overset{b}{C}H_2\overset{c}{C}H_2C{\equiv}\overset{d}{C}SePh$	94	59.45 (59.22)	5.38 (5.42)	a) 1.06 (3 H, t, $J_{ab} \doteq 7$) b) 1.3—1.9 (2 H, m) c) 2.4 (2 H, t, $J_{cb} \doteq 7$) d) 7.0—7.6 (5 H, m)
XIV	$\overset{a}{C}H_3\overset{b}{C}H_2\overset{}{C}H_2\overset{c}{C}H_2C{\equiv}\overset{d}{C}SePh$	93	60.53 (60.79)	5.92 (5.95)	a) 0.7—1.1 (3 H, m) b) 1.3—1.8 (4 H, m) c) 2.2—2.6 (2 H, t) d) 7.0—7.6 (5 H, m)

TABLE 4

$$RC{\equiv}CSePh \xrightarrow{\text{LiAlH}_4} RCH{=}CHSePh$$

	RCH=CHSePh	Yield (%)	Analyses Found (calcd.) (%)		^{1}H NMR data (δ(ppm), J(Hz), TMS internal reference) [a]
			C	H	
Ia	Ph, $\overset{b}{}$; H, $\overset{a}{}$; C=C ; H, $\overset{a}{}$; SePh, $\overset{b}{}$	62	[17]		a) 6.91 (AB quartet, $J = 16$) b) 7.1—7.6 (10 H, m)
VIa	$\overset{a}{C}H_3\overset{b}{C}H_2\overset{c}{C}H_2$, $\overset{e}{}$H; C=C; H$\overset{d}{}$, SePh$\overset{f}{}$	62	58.84 (58.70)	6.25 (6.22)	a) 0.88 (3 H, t, $J_{ab} = 7$) [b, c] b) 1.1—1.7 (2 H, m) c) 2.1 (2 H, q, $J_{cb} = J_{cd} = 7$) d) 5.9 (1 H, dt, $J_{de} = 14$, $J_{dc} = 7$) e) 6.41 (1 H, d, $J_{ed} = 14$) f) 7.0—7.5 (5 H, m)
VIIa	$\overset{a}{C}H_3(\overset{b}{C}H_2)_2\overset{c}{C}H_2$, $\overset{e}{}$H; C=C; H$\overset{d}{}$, SePh$\overset{f}{}$	68	60.51 (60.28)	6.69 (6.69)	a) 0.7—1.0 (3 H, m) [b, c] b) 1.1—1.4 (4 H, m) c) 1.9—2.3 (2 H, m) d) 5.9 (1 H, dt, $J_{dc} = 7$, $J_{de} = 14$) e) 6.41 (1 H, d, $J_{ed} = 14$) f) 7.0—7.5 (5 H, m)

[a] Spectra registered on a XL 100 spectrometer in CCl_4. For IR data see ref. 2a. [b] Spectra registered on a XL 100 spectrometer in $CDCl_3$. [c] IR 950s cm^{-1} (out-of-plane deformation).

The reaction of selenoacetylenes (Table 3) with lithium aluminium hydride in refluxing tetrahydrofuran produced, as expected, vinylic selenides with the *E* configuration (Table 4).

Experimental

Gas liquid chromatographic (GLC) analyses were performed on a Varian 2800 instrument equipped with flame ionization detector and on a CG 2527 gas chromatograph using 5′ × 1/8″ column (of 3% SE 30 or 10% FFAP on 60—80 Chromosorb W″). ^{1}H NMR spectra were recorded on Varian T60 and XL 100 and on Perkin-Elmer R-24A spectrometers, using tetramethylsilane as internal reference. Unless otherwise specified, the spectra were measured in CCl_4 solution. Melting points were determined on a Kofler hot plate and are uncorrected. IR spectra were recorded on Perkin—Elmer 735 and 457-A spectrometers. Selenophenol [29] and diphenyl diselenide [30] were prepared according to literature procedures; phenylselenenyl bromide was generated in situ by reaction of diphenyl diselenide with bromine; 1-phenyl-1-propyne, 1-phenyl-1-butyne, 1-phenyl-1-hexyne and 5-decyne were prepared by procedures previously published [31a,b].

Addition of selenophenol to acetylenes

a) Addition to phenylacetylene. Phenylacetylene (0.50 g, 0.005 mol) was added to selenophenol (0.78 g, 0.005 mol). An exothermic reaction occurred. After 1 h at room temperature, a few ml of ethanol was added to the mixture, causing the product to crystallize. The product was recrystallized from ethanol (for yields and physical data see Tables 1 and 2).

b) Addition to monosubstituted aliphatic acetylenes and to disubstituted acetylenes. The acetylene * (0.0025 mol) was added to selenophenol (0.395 g, 0.0025 mol) in a glass tube. The tube was sealed and the mixture was maintained at room temperature or heated as indicated in Table 1. After the time indicated, the reaction mixture was diluted with hexane, washed with 0.1 *N* NaOH, water and saturated aqueous NaCl, dried with Na_2SO_4 and evaporated. The residual oil was purified by column chromatography on SiO_2 using hexane as eluent. (for yields and physical data see Tables 1 and 2).

Preparation of selenoacetylenes

The acetylene (0.01 mol) in 5 ml THF was treated dropwise (nitrogen atmosphere, 0°C, magnetic stirring) with n-BuLi in hexane (0.01 mol) and after 10 minutes with PhSeBr (2.36 g, 0.01 mol) in 4 ml of THF. The resulting yellow solution was stirred for 1 h at room temperature and treated with saturated NH_4Cl. Hexane was added, the organic layer was washed with saturated NaCl, dried with Na_2SO_4 and evaporated. The residual oil was distilled. (For yields and physical data see Table 3).

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* Freshly distilled acetylene must be used.

Reduction of selenoacetylenes

The selenoacetylene (0.005 mol) was added to LiAlH$_4$ (0.29 g, 0.0075 mol) in 7 ml of THF (room temperature, nitrogen atmosphere, magnetic stirring). The mixture was refluxed for 2 h, treated consecutively with H$_2$O (0.3 ml), NaOH 15% (0.3 ml), H$_2$O (0.9 ml). The crystalline precipitate was removed by filtration and washed with hexane. The filtrate was dried with Na$_2$SO$_4$ and evaporated. The residual oil was purified by column chromatography on SiO$_2$ using hexane as eluent. (For yields and physical data see Table 4).

Acknowledgement

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