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One-pot synthesis of mixed (*Z*)-1,2-bis(organylchalcogene)-1-alkenes precursors of the novel β-organylthio vinyllithium intermediates

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ABSTRACT

One-pot hydrochalcogenation of 1-phenylthioacetylenes using organylselenolate and organyltellurolate anions generated by the insertions of selenium and tellurium in *n*-organyl lithium produced (*Z*)-1,2-bis(organylchalcogene)-1-alkenes. The chemical reactivity of these mixed 1,2-bis(organylchalcogene)-1-alkenes was studied by Te/Li and Se/Li stereoretentive exchanges carried out with *n*-butyl lithium, furnishing the new intermediate species (*Z*)-β-organylthio vinyllithium anions, which were trapped with aldehydes, to give the (*Z*)-3-hydroxy vinyl thioethers with total control of the regio- and stereochemistry.

Stereocontrolled methodologies to prepare vinyl organylchalcogenide compounds and their applications in the construction of new carbon–carbon bonds via organometallic intermediates have been developed with the highest priority.[1] The hydrotelluration described by Buzilova and co-workers[2] stimulated a wide range of studies leading to the synthesis of (*Z*)-vinyl tellurides by addition of organyltellurolate anions to terminal and disubstituted alkynes containing Michael acceptor groups.[1f,3] The chemoselective reactions of sodium tellurolate,[4] selenolate,[5] and thiolate[6] anions occur in conjugated butadyine systems with total control of regio- and stereochemistry, furnishing the (*Z*)-1-organylchalcogene-1-buten-3-ynes. Moreover, (*E*)-vinyl organochalcogenides were obtained by the hydrozirconation of terminal and substituted alkynes using bis(cyclopentadienyl) zirconium (IV) chloride hydride as a reducing agent and subsequent Zr/Te[7], Zr/Se,[8] and Zr/S[9] exchanges. Recently, our group reported the synthesis of (*E*)-vinylsulfides by the hydroalumination of thioacetylenes with lithium di(isobutyl)-*n*-butyl hydride, followed by acid hydrolysis.[10]

Several methods to synthesize 1,1-bis(organylchalcogene)-1-alkenes such as telluroketene acetals,[11] telluro(seleno)ketene acetals,[11a,12] telluro(thio)ketene acetals,[13] and seleno(thio)ketene acetals[14] which could easily lead to the synthesis of trisubstituted olefins containing two heteroatoms attached in the same C-sp^2 position have been developed.

On the other hand, (*Z*)-1,2-bis(organylchalcogene)-1-alkenes were obtained by the hydrochalcogenation of thioacetylenes using the organyltellurolate (RTe^-) and organylselenolate (RSe^-) anions generated 'in situ' by the reduction of diorganyl ditelluride and diorganyl diselenide with sodium borohydride.[15] However, these diorganyl dichalcogenides are known to produce neuropathy to the central nervous system, teratogenic effects, and severe damage to the liver and kidneys.[16] Based on these facts and regarding the applications of (*Z*)-1,2-bis(organylchalcogene)-1-alkenes to the total synthesis of natural products[17] and functionalized alkynyl tellurides, which have shown an interesting antidepressive action.[18] We describe, herein, the one-pot hydrochalcogenation of 1-phenylthioacetylenes **1a–g** in THF/water, using the appropriated chalcogene nucleophilic species,[19] generated 'in situ' by the insertion of elemental tellurium[19a] or selenium[19b] in organyl lithium, avoiding the preliminary preparation and use of volatile, air-sensitive, odorous, and highly toxic diorganyl ditelluride and diorganyl diselenide.[16] The addition of (RSe^-Li^+) or (RTe^-Li^+) anions to thioacetylenes **1a–g** occurred at the β-position relative to the phenylthio group via the vinyl intermediate type **2** furnishing the mixed (*Z*)-1,2-bis(organylchalcogene)-1-alkenes **3a–m** in good yields (Table 1).

As a representative example of this protocol, we performed the hydrotelluration of 1-phenylthio-1-hexyne **1b** (1.5 equiv) with the lithium butyltellurolate anion [(C_4H_9TeLi),[19a] 1.5 equiv, generated 'in situ' by insertion of tellurium (1.5 equiv) in *n*-BuLi (1.5 equiv)] in THF (6.0 mL) followed by the addition of water (4.0 mL) and

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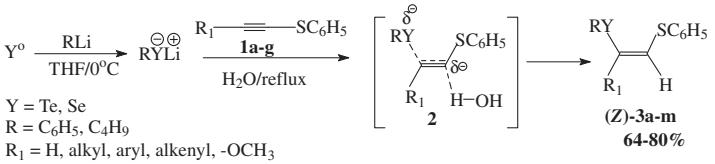
Table 1
Synthesis of (***Z***)-1,2-bis(organylchalcogene)-1-alkenes



Y = Te, Se
R = C_6H_5, C_4H_9
R_1 = H, alkyl, aryl, alkenyl, -OCH_3

Entry	Thioacetylene	Nucleophile	Product[a]	Time (h)	Yield[b] (%)
1	H—≡—SC_6H_5 **1a**	C_4H_9TeLi	C_6H_5S, TeC_4H_9 **3a**	1.5	80
2	C_4H_9—≡—SC_6H_5 **1b**	C_4H_9TeLi	C_6H_5S, TeC_4H_9, C_4H_9 **3b**	2.5	76
3	C_7H_{15}—≡—SC_6H_5 **1c**	C_4H_9TeLi	C_6H_5S, TeC_4H_9, C_7H_{15} **3c**	2.5	73
4	C_6H_5—≡—SC_6H_5 **1d**	C_4H_9TeLi	C_6H_5S, TeC_4H_9, C_6H_5 **3d**	1.5	80
5	CH_3O—≡—SC_6H_5 **1e**	C_4H_9TeLi	C_6H_5S, TeC_4H_9, OCH_3 **3e**	1.5	75
6	⬡—≡—SC_6H_5 **1f**	C_4H_9TeLi	C_6H_5S, TeC_4H_9, ⬡ **3f**	2.0	73
7	C_4H_9—≡—SC_6H_5 **1b**	C_6H_5TeLi	C_6H_5S, TeC_6H_5, C_4H_9 **3g**	3.5	75
8	C_6H_5—≡—SC_6H_5 **1d**	C_6H_5TeLi	C_6H_5S, TeC_6H_5, C_6H_5 **3h**	3.0	73
9	C_4H_9—≡—SC_6H_5 **1b**	C_6H_5SeLi	C_6H_5S, SeC_6H_5, C_4H_9 **3i**	4.0	78
10	$C_{10}H_{21}$—≡—SC_6H_5 **1g**	C_6H_5SeLi	C_6H_5S, SeC_6H_5, $C_{10}H_{21}$ **3j**	4.0	64
11	C_6H_5—≡—SC_6H_5 **1d**	C_6H_5SeLi	C_6H_5S, SeC_6H_5, C_6H_5 **3k**	3.5	73
12	CH_3O—≡—SC_6H_5 **1e**	C_6H_5SeLi	C_6H_5S, SeC_6H_5, OCH_3 **3l**	4.0	70
13	⬡—≡—SC_6H_5 **1f**	C_6H_5SeLi	C_6H_5S, SeC_6H_5, ⬡ **3m**	4.0	68

[a] Fully characterized by NMR (^1H, ^{13}C, gNOESY), MS, microanalysis data.
[b] Isolated yields after purification by chromatography using silica gel (230–400 mesh) and hexane as the mobile phase in all cases.