Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters 49 (2008) 3872–3876
Tetrahedron Letters

Hydroalumination of selenoacetylenes: a versatile generation and reactions of α-aluminate vinyl selenide intermediates in the highly regio and stereoselective synthesis of telluro(seleno)ketene acetals

Palimécio G. Guerrero Jr. [a,*], Miguel J. Dabdoub [b], Adriano C. M. Baroni [c]

[a] *Laboratório de Química Orgânica, Universidade Estadual Paulista, UNESP, Tamekishi Takano, 5, 11900-000 Registro, SP, Brazil*
[b] *Laboratório de Compostos Organocalcogênios, Universidade de São Paulo/USP, Av. Bandeirantes, 3900, 14500-000 Ribeirão Preto, SP, Brazil*
[c] *Laboratório de Química Farmacêutica, Universidade Federal do Mato Grosso do Sul, UFMS, Campo Grande, MS, Brazil*

Received 15 February 2008; revised 2 April 2008; accepted 10 April 2008
Available online 15 April 2008

Abstract

The hydroalumination of butylseleno acetylenes with DIBAL-H followed by addition of *n*-butyllithium generated in situ the (*Z*)-butylseleno vinyl alanates intermediates which were captured with C_4H_9TeBr furnishing the (*E*)-telluro(seleno)ketene acetals exclusively. The isomers with opposite stereochemistry (*Z*)-telluro(seleno)ketene acetals were obtained by the reduction of phenylseleno acetylenes with lithium di-(isobutyl)-*n*-butyl aluminate hydride (Zweifel's reagent) followed by reaction of (*E*)-phenylseleno vinyl alanates intermediates with C_4H_9TeBr.

In recent decades organoselenium[1] and organotellurium[2] chemistries have become promising research fields leading to the development of new reagents with many applications in organic synthesis. Vinyl tellurides[3] have attracted significant attention and interest because these compounds can be used as electrophilic or nucleophilic sp^2 carbon sources in different carbon–carbon formation processes including synthesis of natural products.[4] Moreover, stereo-retentive transmetallations represented by Te/Li,[5] Te/Cu[4a] and Te/Zn[6] were developed mainly for their application as precursors in chain elongation.

The synthesis of chalcogeno(ketene) acetals and their use in the preparation of highly functionalised vinylmetallic reagents is also of interest because carbon–carbon or carbon-heteroatom bond formation of these organometallics affords polyfunctionalised olefins.[7,8] Our group developed methodologies to obtain compounds containing two organochalcogens groups attached at one double bond. Telluroketene acetals[9] were obtained by reaction of telluroacetylenes with bis(cyclopentadienyl)chloro zirconium hydride (Schwartz's reagent) followed by addition of C_4H_9TeBr. Also, the stereoselective synthesis of (*E*)- and (*Z*)-telluro(thio)ketene acetals[10] was effected by the reaction of phenylthio acetylenes with organoaluminium hydrides as reducing agents and subsequent treatment of the vinyl alanates intermediates with C_4H_9TeBr.

Few methodologies to obtain telluro(seleno)ketene acetals have been published.[9,11,12] The reaction of DIBAL-H **1** and phenylseleno acetylenes followed by addition of electrophilic tellurium species furnished the (*E*)-telluro(seleno)ketene acetals.[11] However, the products desired were obtained in low to moderate yields (22–50%) because the Al/Te exchange reactions occurred with lower efficiency in α-phenylseleno vinyl alanas intermediates.[11]

More recently, we described the 'one pot'preparation of (*E*)-telluro(seleno)ketene acetals via hydrozirconation of alkynyl selenolate anions.[12] Using this reaction it is possible only to obtain the (*E*)-telluro(seleno)ketene acetals compounds.[12] To the best of our knowledge,

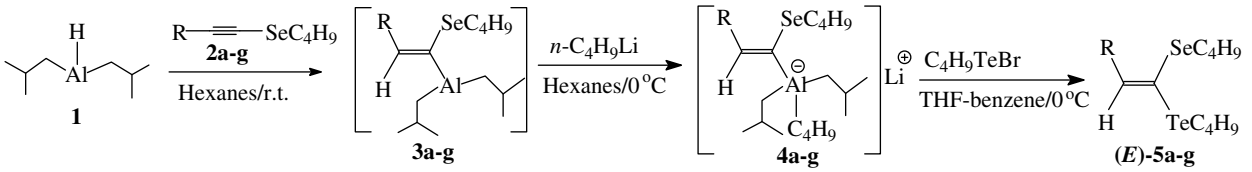
* Corresponding author. Tel.: +55 13 38225793.
E-mail address: pali@registro.unesp.br (P. G. Guerrero Jr.).

0040-4039/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2008.04.072

methodologies to synthesise (*Z*)-telluro(seleno)ketene acetals with high stereoselectivity have not yet been published.

We report here a new, general and highly regio and stereoselective synthesis of (*Z*)- and (*E*)-telluro(seleno)ketene acetals employing the hydroalumination of selenoacetylenes. Reactions involving DIBAL-H **1** (1.0 mmol) and butylseleno acetylenes **2a–g** (1.0 mmol) in hexanes (5 mL) at room temperature, occurred with *cis*-addition of hydride at the triple bond and transference of the organoaluminium moiety to the carbon sp^2 terminal afforded the (*Z*)-butylseleno vinyl alanas intermediates **3a–g**, which were treated with *n*-butyllithium (1.0 mmol) to give the (*Z*)-butylseleno vinyl alanates **4a–g**.

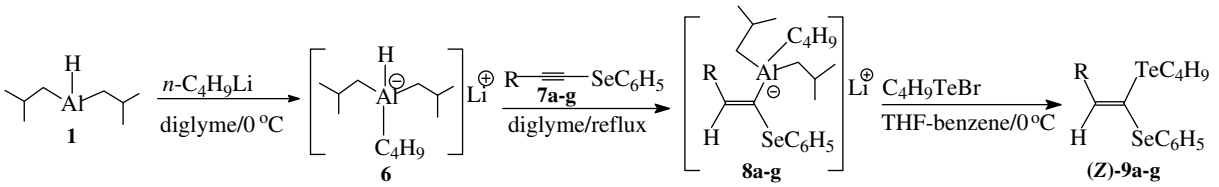
Table 1
Synthesis of (*E*)-telluro(seleno)ketene acetals

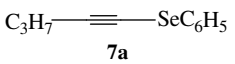
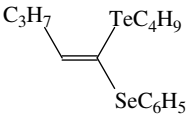
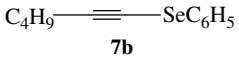
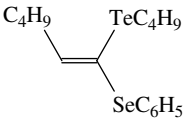
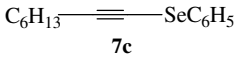
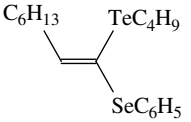
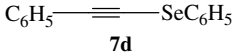
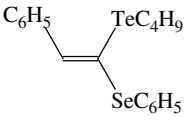
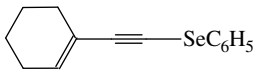
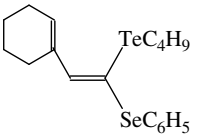
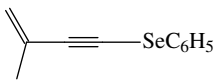
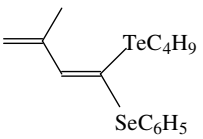
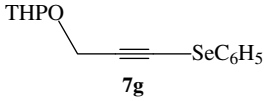
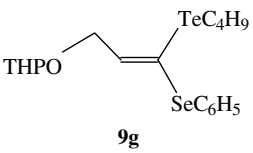


Entry	Butylseleno acetylenes	Products[a]	Time reaction[b] (h)	Yield[c] (%)
1	C_3H_7—≡—SeC_4H_9 **2a**	C_3H_7, SeC_4H_9, TeC_4H_9 **5a**	2.0	85
2	C_4H_9—≡—SeC_4H_9 **2b**	C_4H_9, SeC_4H_9, TeC_4H_9 **5b**	2.5	87
3	C_6H_{13}—≡—SeC_4H_9 **2c**	C_6H_{13}, SeC_4H_9, TeC_4H_9 **5c**	2.5	80
4	C_6H_5—≡—SeC_4H_9 **2d**	C_6H_5, SeC_4H_9, TeC_4H_9 **5d**	3.0	76
5	≡—SeC_4H_9 **2e**	SeC_4H_9, TeC_4H_9 **5e**	2.5	75
6	≡—SeC_4H_9 **2f**	SeC_4H_9, TeC_4H_9 **5f**	2.5	70
7	THPO—≡—SeC_4H_9 **2g**	SeC_4H_9, THPO, TeC_4H_9 **5g**	2.0	76

[a] Fully characterised by NMR, MS, Microanalyses data.
[b] Formation of intermediates **3a–g**.
[c] Isolated yields after purification by chromatography using silica flash (230–400mesh) and hexane as the eluent for compounds **5a–f** and a mixture of ethyl acetate:hexane (2:8) for **5g**.

Table 2
Synthesis of (*Z*)-telluro(seleno)ketene acetals



Entry	Phenylseleno acetylenes	Products[a]	Time reaction[b] (h)	Yield[c] (%)
1	 **7a**	 **9a**	1.5	89
2	 **7b**	 **9b**	1.5	80
3	 **7c**	 **9c**	2.0	78
4	 **7d**	 **9d**	2.5	76
5	 **7e**	 **9e**	2.5	75
6	 **7f**	 **9f**	2.0	72
7	 **7g**	 **9g**	1.5	71

[a] Fully characterised by NMR, MS, Microanalyses data.
[b] Formation of intermediates **8a–g**.
[c] Isolated yields after purification by chromatography using silica flash (230–400 mesh) and hexane as the eluent for compounds **9a–f** and a mixture of ethyl acetate:hexane (2:8) for **9g**.

Finally, these vinyl alanate intermediates were captured with C_4H_9TeBr (4.0 mmol) in THF/benzene at 0 °C furnishing exclusively the (*E*)-1-butyltelluro-1-butylseleno-2-organoyl ethenes **5a–g**[13] with good yields (Table 1).

The stereochemistry of the (*E*)-telluro(seleno)ketene acetals was determined by the gNOESY in the ^1H NMR spectra of **5b**. An enhancement of the methylenic protons next to tellurium was observed as the vinylic proton of **5b** was irradiated.

The NOE effect was also observed between the allylic protons and the CH_2 of the butylseleno group. Futhermore, correlations were not observed between the vinylic hydrogen and the CH_2 attached at the selenium atom. These NMR experiments indicate that the butylseleno group is situated close to the alkyl group attached to the adjacent carbon (*E* configuration).

In the context of our strong interest in exploring a convenient access to (*Z*)-telluro(seleno)ketene acetals we studied the hydroalumination of butylseleno acetylenes using the lithium di-(isobutyl)-*n*-butyl aluminate hydride **6** (Zweifel's reagent)[14] obtained 'in situ' by the addition of *n*-butyllithium (1.0 equiv) to a solution of DIBAL-H (1.0 equiv.) in diglyme (10 mL) at 0 °C.

The first attempt at *trans*-stereoselective reaction of the 1-selenobutyl-1-hexyne **2b** failed, and the hydroalumination afforded a mixture of alkylselenides as product due to C_{sp-Se} cleavage from the starting material.

However, when we reacted the phenylseleno acetylenes (1.0 mmol.) **7a–g** and lithium di-(isobutyl)-*n*-butyl aluminate hydride **6** (1.5 mmol) in diglyme (10 mL) under reflux, the (*E*)-phenylseleno vinyl alanate intermediates **8a–g** were generated by the *anti*-addition of the hydride from Zweifel's reagent to the triple bond.

Consequently, the organoaluminium moiety was transferred to the carbon sp^2 bearing the phenylseleno group and finally these intermediates **8a–g** were trapped with C_4H_9TeBr furnishing the (*Z*)-telluro(seleno)ketene acetals **9a–g**[15] exclusively and good yields (Table 2).

The stereochemistry of the (*Z*)-telluro(seleno)ketene acetals was also determined by the gNOESY experiments. For example we utilised compound **9c** to demonstrate the (*Z*)-configuration of the trisubstituted olefins **9a–g**. NOE effects from allylic CH_2 to the CH_2 directly attached to the tellurium atom and between vinyl hydrogen and CH aromatic from phenyl group bonded to the selenium atom were observed. On the other hand, correlations were not observed between the vinylic hydrogen and CH_2 bonded directly at the tellurium atom.

In summary, we developed two new methodologies that permit the exclusive synthesis of (*E*)- and (*Z*)-telluro(seleno)ketene acetals with total control of regio and stereochemistry. The vinyl aluminates complexes described here for the first time are responsible for the stereospecificity of tellurium compounds formation which were obtained by NOE experiments. Synthetic applications involving the Te/Li exchange and cross coupling reactions of these telluro(seleno)ketene acetals are under development in our laboratory.

Acknowledgments

The authors thank to FAPESP and FUNDUNESP for financial support and Dr. Janet W. Reid (J.W.R. Associates) for revising the English text.

References and notes

1. (a) Wirth, T. *Organoselenium Chemistry, Modern Developments in Organic Synthesis*, Vol. 208; Springer: Berlin, **2000**; (b) Denmark, S. E.; Edwards, M. G. *J. Org. Chem.* **2006**, *71*, 7293.
2. (a) Petragnani, N. *Best Synthetic Methods — Tellurium in Organic Synthesis*; Academic Press: London, 1994; (b) Petragnani, N.; Stefani, H. A. *Tetrahedron* **2005**, *61*, 1613.
3. (a) Comasseto, J. V.; Ling, L. W.; Petragnani, N.; Stefani, H. A. *Synthesis* **1997**, 373; (b) Yang, J.; Cohn, S. T.; Romo, D. *Org. Lett.* **2000**, *2*, 763; (c) Dabdoub, M. J.; Rotta, J. C. *Synlett* **1996**, 526; (d) Barrientos-Astigarraga, R. E.; Castelani, P.; Comasseto, J. V.; Formiga, H. B.; Da Silva, N. C.; Sumida, C. Y.; Vieira, M. L. *J. Organomet. Chem.* **2001**, *623*, 43.
4. (a) Marino, J. P.; McClure, M. S.; Holub, D. P.; Comasseto, J. V.; Tucci, F. C. *J. Am. Chem. Soc.* **2002**, *124*, 1664; (b) Oliveira, J. M.; Zeni, G.; Malvestiti, I.; Menezes, P. H. *Tetrahedron Lett.* **2006**, *47*, 8183.
5. (a) Hiiro, T.; Mogami, T.; Kambe, N.; Fujiwara, S. I.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1187; (b) Dabdoub, M. J.; Dabdoub, V. B. *Tetrahedron* **1995**, *51*, 9830.
6. (a) Dabdoub, M. J.; Dabdoub, V. B.; Marino, J. P. *Tetrahedron Lett.* **2000**, *41*, 433; (b) Dabdoub, M. J.; Dabdoub, V. B.; Marino, J. P. *Tetrahedron Lett.* **2000**, *41*, 437.
7. Larock, R. C. *Comprehensive Organic Transformations*; VCH: New York, 1989.
8. Yoshimatsu, M.; Oguri, K.; Ikeda, K.; Gotoh, S. *J. Org. Chem.* **1998**, *63*, 4475.
9. Dabdoub, M. J.; Begnini, M. L.; Guerrero, P. G., Jr. *Tetrahedron* **1998**, *54*, 2371.
10. Dabdoub, M. J.; Guerrero, P. G., Jr. *Tetrahedron Lett.* **2001**, *42*, 7167.
11. Dabdoub, M. J.; Cassol, T. M.; Barbosa, S. L. *Tetrahedron Lett.* **1996**, *37*, 831.
12. Dabdoub, M. J.; Begnini, M. L.; Guerrero, P. G., Jr.; Baroni, A. C. M. *J. Org. Chem.* **2000**, *65*, 61.
13. *Typical procedure for the synthesis of (E)-telluro(seleno)ketene acetals 5a–g:* To a solution of butylseleno acetylene (1.0 mmol) in hexanes (5 mL) under a nitrogen atmosphere, DIBAL-H (1.5 mL; 1.0 mmol; 1.5 M in toluene) was added at room temperature and stirred for the time shown in Table 1. The mixture was cooled at 0 °C, *n*-butyllithium (0.4 mL; 1.0 mmol; 2.5 M in hexanes) was added dropwise and the reaction was stirred for 30 min. Then, a solution of C_4H_9TeBr prepared separately [4.0 mmol; by the addition of Br_2 (0.32 g, 2.0 mmol) in benzene (10 mL) to a solution of $(C_4H_9Te)_2$ (2.0 mmol, 0.73 g) in THF (10 mL) at 0 °C] was transferred via syringe. Stirring was continued for an additional 30 min and the solution was diluted with ethyl acetate (100 mL), the organic phase washed with brine (3 × 50 mL), dried over anhydrous $MgSO_4$, and the solvent evaporated under vacuum. The residue containing the (*E*)-telluro(seleno)-ketene acetals was obtained as a yellow liquid after purification by silica flash (230–400 mesh). *(E)-1-Butyltelluro-1-butylseleno-1-hexene* **5b**. Yield: 87% (0.35 g); GC/MS *m/z* 402 (5.65), 279 (10.2), 267 (11.5), 202 (16.4),149 (90.1), 83 (17.2), 81 (98.9), 57 (100.0); ^1H NMR (300 MHz) (δ in $CDCl_3$) 0.85–0.95 (m, 9H), 1.3–1.5 (m, 8H), 1.62 (quint, $J = 7.3$ Hz, 2H), 1.78 (quint, $J = 7.0$ Hz, 2H), 2.33 (q, $J = 7.3$ Hz, 2H), 2.73 (t, $J = 7.3$ Hz, 2H), 2.79 (t, $J = 7.3$ Hz, 2H),

6.68 (t, $J = 7.3$ Hz, 1H); ^{13}C NMR 10.1, 13.4, 13.6, 13.8, 22.1, 22.8, 25.0, 31.0, 31.1, 32.4, 33.5, 34.3, 97.8, 151.6; Anal. Calcd for $C_{14}H_{28}TeSe$: C, 41.73; H, 7.00. Found: C, 41.90; H, 6.56.

14. (a) Zweifel, G.; Lynd, R. A.; Murray, R. E. *Synthesis* **1977**, 52; (b) Miller, J. A.; Leong, W.; Zweifel, G. *J. Org. Chem.* **1988**, *53*, 1839.
15. *Typical procedure for the synthesis of (Z)-telluro(seleno) ketene acetals* **9a–g**. To a solution of DIBAL-H (1.0 mL; 1.5 mmol; 1.5 M in toluene) in diglyme (5 mL), under a nitrogen atmosphere, *n*-butyllithium (0.6 mL; 1.5 mmol; 2.5 M in hexanes) was added dropwise at 0 °C and the solution stirred for 30 min. After this period a solution of phenylseleno acetylene (1.0 mmol) in diglyme (5 mL) was added via syringe and the mixture refluxed for the time indicated in Table 2. Next, a solution of C_4H_9TeBr (4.0 mmol; prepared separately as described above) was transferred with a syringe and stirring continued for another 30 min. The solution was diluted with ethyl acetate (100 mL), the organic phase washed with brine (3×50 mL), dried over anhydrous $MgSO_4$ and the solvent evaporated under vacuum. The residue containing the (*Z*)-telluro(seleno)ketene acetals was obtained as a yellow liquid after purification by silica flash (230–400 mesh). (*Z*)-1-Butyltelluro-1-phenylseleno-1-octene **9c**: Yield: 78% (0.35 g) GC/MS *m*/*z* 450 (4.35), 405 (9.12), 110 (100.0), 57 (36.07); ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 0.84–0.91 (m, 6H), 1.2–1.5 (m, 10H), 1.61 (quint, $J = 7.3$ Hz, 2H), 2.21 (q, $J = 7.3$ Hz, 2H), 2.78 (t, $J = 7.3$ Hz, 2H), 6.46 (t, $J = 7.3$ Hz, 1H), 7.31–7.51 (m, 5H); ^{13}C NMR 10.9, 13.4, 14.0, 22.5, 25.0, 28.7, 28.8, 31.6, 34.0, 37.5, 98.2, 127.0, 128.3, 129.1, 130.5, 132.2, 132.8, 149.5. Anal. Calcd for $C_{18}H_{28}TeSe$: C, 48.00; H, 6.26. Found: C, 48.34; H, 6.38.