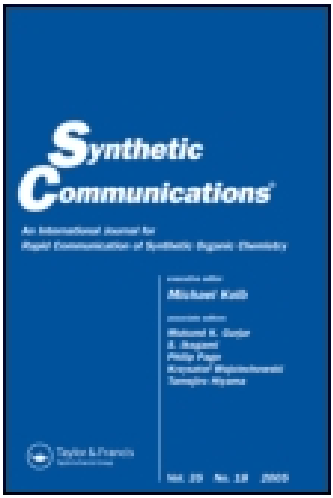

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Hydroalumination of Thioacetylenes: A Versatile Generation and Reactions of α-Aluminate Sulfides Intermediates

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Abstract: Hydroalumination of thioacetylenes using DIBAL-H and lithium di-(isobutyl)-n-(butyl)-aluminate hydride (Zweifel's reagent), followed by addition of water, furnished exclusively the (**Z**)- and (***E***)-vinyl sulfides, respectively. The regio- and stereochemistry of the intermediates generated, (**Z**)- and (***E***)-phenylthio vinyl alanates, were determined by capture with iodine, which afforded the corresponding (***E***)- and (**Z**)-1-iodo-1-phenylthio-2-organoyl ethenes. Reactions of the (***E***)-iodo(thio)ketene acetals with n-BuLi followed by addition of hexanal afforded the (**Z**)-phenylthio allylic alcohol, while the (**Z**)-iodo(thio)ketene acetals under similar reactions conditions gave the (***E***)-phenylthio allylic alcohol exclusively.

Keywords: Hydroalumination, phenylthio allylic alcohol, regiochemistry, thio(iodo)ketene acetals, vinyl alanates, vinyl sulfides

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INTRODUCTION

Among the organochalcogene species, vinyl sulfides have attracted interest because they can be used as important intermediates in organic synthesis.[1] These compounds have been used in the preparation of substituted olefines by a cross-coupling reaction with Grignard reagents,[2,3] as well as in the synthesis of bioactive molecules.[4] The vinyl sulfide moiety is found in many natural products with interesting biological properties.[5] Considering the application of vinyl sulfides[6] in organic synthesis, few methods described obtaining (**Z**)- and (***E***)-vinyl sulfides derivatives with high stereoselectivity.[1,3,6b]

Moreover, α-halo vinyl sulfides have emerged as interesting intermediates, which are used to prepare a wide range of polyfunctionalized olefines via a cross-coupling reaction catalyzed by transition metals.[7] However, very few articles[7,8] described their preparation, and a general method to synthesize (**Z**)- and (***E***)-α-halo vinyl sulfides with total control of regio- and stereoselectivity has not yet been reported to the best of our knowledge.

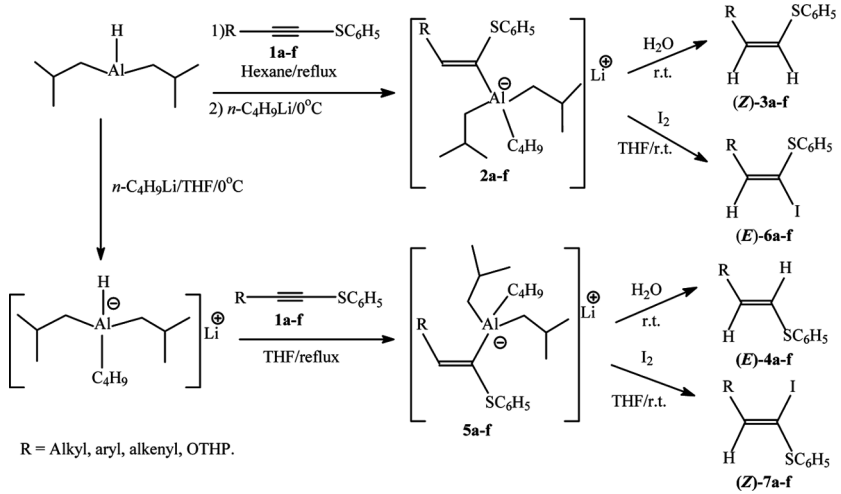
RESULTS AND DISCUSSION

Here we describe the first synthesis of (**Z**)- and (***E***)-vinyl sulfides and the corresponding (**Z**)- and (***E***)-iodo(thio)ketene acetals with high regio- and stereoselectivity, applying as the key step the hydroalumination of thioacetylenes.

The addition of diisobutylaluminum hydride (DIBAL-H) to the triple bonds of thioacetylenes **1a–f** followed by *n*-BuLi at 0 °C afforded the (**Z**)-phenylthio vinyl alanates **2a–f** intermediates, which then were treated with water to give exclusively the (**Z**)-phenylthio alkenes **3a-f** (Scheme 1, Table 1). Synthesis of isomers with the opposite stereochemistry, (***E***)-vinyl sulfides **4a–f**, was carried out employing lithium di-(isobutyl)-*n*-(butyl) aluminate hydride (Zweifel's reagent).[9] This interesting "ate" complex was generated in situ by the reaction of *n*-BuLi (1.0 equiv.) and DIBAL-H (1.0 equiv.) in tetrahydrofuran (THF) at 0 °C, which was inserted in an *anti*-fashion into thioacetylenes **1a–f** leading to the formation of the (***E***)-phenylthio vinyl alanates **5a–f**, These intermediates were trapped with water, furnishing exclusively the (***E***)-vinyl sulfides **4a–f** (Scheme 1, Table 1).

The stereochemistry of the (**Z**)- and (***E***)-vinyl sulfides was determined by ^{1}H NMR experiments, considering the coupling constant value of the vinylic hydrogen, in the ranges of 10.0–10.5 Hz and 14.5–15.0 Hz, respectively.

Vinyl compounds containing two heteroatoms attached to the same sp^2 carbon such as telluroketene acetals,[10] telluro(seleno)ketene



Scheme 1. Hydroalumination of thioacetylenes.

acetals,[11] and seleno(halo)ketene acetals[12] have previously been prepared and are used as versatile intermediates in organic synthesis.

Within the context of our strong interest in exploring a convenient access to telluro(thio)ketene acetals with high regio- and stereoselectivity, we developed the *syn* and *anti*-hydroalumination of thioacetylenes.[13] However, the capture of the (***E***)-phenylthio vinyl alanate intermediate with C_4H_9TeBr led to a stereoisomeric mixture of the (**Z**)- and (***E***)-telluro(thio)ketene acetals.[13] These results, combined with the total retention of configuration involving the capture of phenylthio alanates **2** and **5** with water (Scheme 1), prompted us to study the chemical reactivity of these intermediates with other electrophiles.

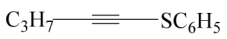
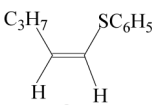
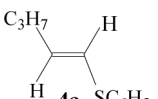
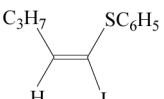
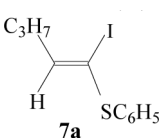
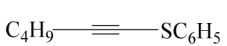
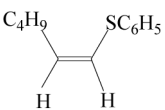
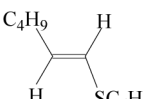
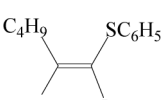
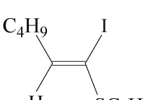
In this way, the capture of the intermediates phenylthio vinyl alanates **2a–f** and **5a–f** with iodine furnished, respectively, the (***E***)- and (**Z**)-1-iodo-1-phenylthio-2-organoyl ethenes **6a–f** and **7a–f**, exclusively and in good yields (Scheme 1).

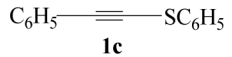
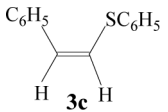
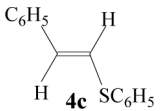
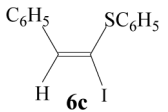
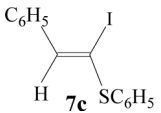
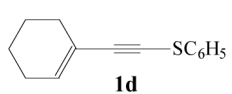
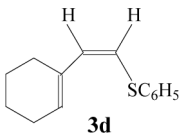
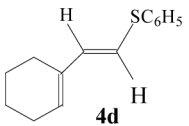
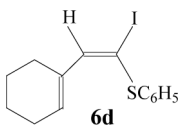
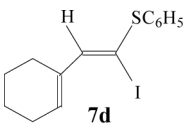
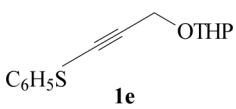
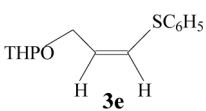
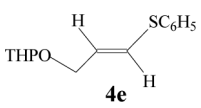
Trisubstituted olefins, calcogeno(thio)ketene acetals and calcogeno-(halo)ketene acetals, are important reagents and intermediates, which can be applied to the formation of carbon–carbon bonds.[14]

We have previously reported the Te/Li exchange using telluro(thio)-ketene acetals and subsequent reaction with aldehyde.[13] However, a stereoisomeric mixture of the phenylthio allylic alcohols was obtained when the reaction was performed with (***E***)-telluro(thio)ketene acetals.[13]

Now, we describe our preliminary results to demonstrate the synthetic utility of (**Z**)- and (***E***)-iodo(thio)ketene acetals. The reaction of the

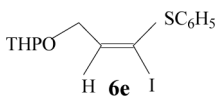
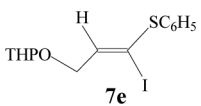
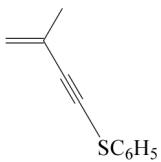
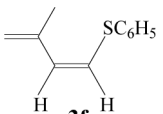
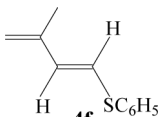
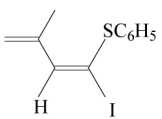
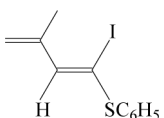
Table 1. Synthesis of vinyl sulfides and iodo(ketene) acetals

Thioacetylene	Reaction time (min.)[a]	Product[b]	Yield[c]	Reaction time (min.)[d]	Product[b]	Yield[c]
 **1a**	50	 **3a**	94	60	 **4a**	80
		 **6a**	80		 **7a**	78
 **1b**	45	 **3b**	93	60	 **4b**	79
		 **6b**	79		 **7b**	81

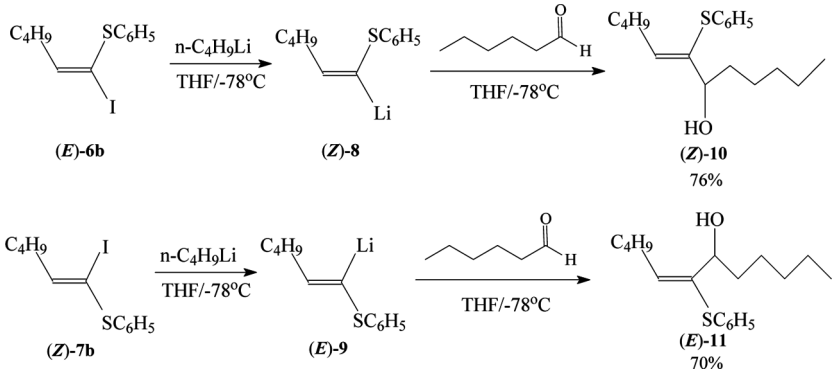
 **1c**	30	 **3c**	93	40	 **4c**	74
		 **6c**	75		 **7c**	70
 **1d**	60	 **3d**	74		 **4d**	75
		 **6d**	70	40	 **7d**	69
 **1e**	45	 **3e**	75		 **4e**	65

(*Continued*)

Table . Continued

Thioacetylene	Reaction time (min.)[a]	Product[b]	Yield[c]	Reaction time (min.)[d]	Product[b]	Yield[c]
		 **6e**	65	60	 **7e**	60
 **1f**	50	 **3f**	70		 **4f**	67
		 **6f**	60	55	 **7f**	65

[a]Formation of (**Z**)-vinyl alanates **2a–f** intermediates.
[b]Fully characterized by NMR, NOESY, MS.
[c]Isolated yields of the products purified by flash chromatography on silica gel.
[d]Formation of (***E***)-vinyl alanates **5a–f** intermediates.



Scheme 2. Generation of (***Z***)- and (***E***)-α-lithiated vinyl sulfides.

isomerically pure (***E***)- and (**Z**)-1-iodo-1-thiophenyl-1-hexene **6b** and **7b** (1.0 equiv.) with *n*-BuLi (1.1 equiv.) at −78 °C afforded the corresponding (**Z**)- and (***E***)-α-lithiated vinyl sulfides **8** and **9**. These intermediates were trapped with hexanal (1.2 equiv.), furnishing the (**Z**)- and (***E***)-6-phenylthio-5-dodecen-7-ol **10** and **11**, respectively, with total retention of configuration and good yields (Scheme 2). Direct condensation of phenylthio vinyl alanates **2** and **5** intermediates with hexanal did not occur. Thus, it was necessary to convert these intermediates into the iodine derivatives and to effect the I/Li exchange before carrying out the reaction with the aldehyde.

In conclusion, we have developed new and efficient methodologies to afford (**Z**)- and (***E***)-vinyl sulfides exclusively by the hydroalumination of thioacetylenes using DIBAL-H and Zweifel's reagent as the key step. By using iodine instead of water as the electrophiles, we successfully prepared the corresponding (***E***)- and (**Z**)-iodo(thio)ketene acetals with total regio- and stereo-control. The I/Li exchange reaction involving the isomerically pure (**Z**)- and (***E***)-iodo(thio)ketene acetals, described here for the first time, allowed us to obtain (***E***)- and (**Z**)-phenylthioallylic alcohols with total retention of stereochemistry.

EXPERIMENTAL

General Procedure for the Preparation of (Z)-Vinyl Sulfides

A solution of thioacetylene (1.0 mmol) in hexanes (2.0 mL) was added to a flask containing a solution of DIBAL-H (2.0 mL, 2.0 mmol, 1.0 M in hexanes) in hexanes (10 mL) under N_2 at room temperature, and the mixture was stirred under reflux (reaction time shown in Table 1). The

solution was cooled to 0 °C, and then *n*-BuLi (1.53 mL, 2.0 mmol, 1.3 M in hexanes) was added dropwise. Stirring continued for 30 min. After this time, the mixture reached the room temperature, and water (5.0 mL) was transferred to the flask via syringe. The products were extracted with ethyl acetate (100 mL); the organic phase was washed with brine (3×50 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (230–400 mesh) using hexane as mobile phase in all cases, to give the corresponding (**Z**)-vinyl sulfides as yellow oil.

Data

(**Z**)-1-Phenylthio-1-pentene **3a**

Yield: 94% (0.16 g). ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 0.9 (t, $J = 7.5$ Hz, 3H), 1.4 (m, 2H), 2.2 (dt, $J = 9.0$ Hz, $J = 7.5$ Hz, 2H), 6.0 (dt, $J = 9.0$ Hz, $J = 7.5$ Hz, 1H), 6.4 (d, $J = 10.0$ Hz, 1H), 7.1–7.5 (m, 5H); ^{13}C NMR (20 MHz) (δ in $CDCl_3$) 12.3, 22.0, 30.1, 125.5, 126.5, 128.5, 129.7, 135.0, 135.9, 138.7, 138.9. Anal. calc. for $C_{11}H_{14}S$: C, 74.10; H, 7.81. Found: C, 73.91; H, 7.65.

(**Z**)-1-Phenylthio-1-hexene **3b**

Yield: 93% (0.18 g). ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 1.0 (t, $J = 7.5$ Hz, 3H), 1.1–1.5 (m, 4H), 2.3 (dt, $J = 9.0$ Hz, $J = 7.5$ Hz, 2H), 5.8 (dt, $J = 9.0$ Hz, 1H), 6.3 (d, $J = 10.0$ Hz, 1H), 7.1–7.4 (m, 5H); ^{13}C NMR (20 MHz) (δ in $CDCl_3$) 12.4, 22.2, 29.1, 30.2, 125.3, 126.4, 128.7, 129.8, 135.3, 135.7, 138.6, 138.9. Anal. calc. for $C_{12}H_{16}S$: C, 75.11; H, 8.38. Found: C, 75.13; H, 8.45.

(**Z**)-1-Phenylthio-2-phenyl Ethene **3c**

Yield: 93% (0.19 g). ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 6.4 (d, $J = 10.0$ Hz, 1H), 6.6 (d, $J = 10.0$ Hz, 1H), 7.5 (m, 10H); ^{13}C NMR (20 MHz) (δ in $CDCl_3$) 124.3, 124.5, 125.0, 125.5, 126.4, 126.8, 128.5, 128.7, 129.6, 130.4, 131.3, 132.5, 135.8, 138.9. Anal. calc. for $C_{14}H_{12}S$: C, 79.22; H, 5.65. Found: C, 78.82; H, 5.43.

(**Z**)-1-Phenylthio-2-cyclohexenyl Ethene **3d**

Yield: 74% (0.16 g). ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 1.5–2.1 (m, 8H), 5.7 (m, 1H), 6.1 (d, $J = 10.0$ Hz, 1H), 6.3 (d, $J = 10.0$ Hz, 1H), 7.2 (m, 5H); ^{13}C NMR (20 MHz) (δ in $CDCl_3$) 21.5, 22.3, 23.1, 24.5, 128.5, 128.7,

129.3, 130.4, 131.5, 135.1, 135.8, 138.5, 139.4, 140.2. Anal. calc. for $C_{14}H_{16}S$: C, 77.72; H, 7.42. Found: C, 77.73; H, 7.25.

(**Z**)-1-Phenylthio-3-tetrahydropyranyl-1-propene **3e**

Yield: 75% (0.18 g). ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 1.65 (br, THP methylenes), 3.5 (d, $J = 7.5$ Hz, 2H), 6.0 (dt, $J = 10.5$ Hz, $J = 7.5$ Hz, 1H), 6.4 (d, $J = 10.5$ Hz, 1H), 7.3 (m, 5H); ^{13}C NMR (75 MHz) (δ in $CDCl_3$) 10.6, 13.4, 21.8, 30.9, 58.6, 73.6, 126.3, 126.7, 127.3, 128.9, 132.3, 134.7, 139.6, 140.2. Anal. calc. for $C_{14}H_{18}SO_2$: C, 67.20; H, 7.20. Found: C, 67.00; H, 7.40.

(**Z**)-1-Phenylthio-3-methyl-1,3-butadiene **3f**

Yield: 70% (0.12 g). 1H NMR (300 MHz) (δ in CDCl3) 0.9 (t, $J = 7.5$ Hz, 3H), 5.1 (q, $J = 1.0$ Hz, 1H), 5.2 (s, 1H), 6.6 (d, $J = 10.0$ Hz, 1H), 6.8 (d, $J = 10.0$ Hz, 1H), 7.3 (m, 5H); ^{13}C NMR (75 MHz) (δ in $CDCl_3$) 13.4, 103.1, 112.3, 126.5, 127.6, 128.6, 132.4, 128.3, 138.3, 139.4, 145.8. Anal. calc. for $C_{11}H_{12}S$: C, 75.00; H 6.91. Found: C, 74.81; H, 6.74.

General Procedure for the Preparation of (*E*)-Iodo(thio)ketene Acetals

A solution of thioacetylene (1.0 mmol) in hexanes (2.0 mL) was added to a flask containing a solution of DIBAL-H (2.0 mL, 2.0 mmol, 1.0 M in hexanes) in hexanes (10 mL) under N_2 at room temperature, and the mixture was stirred under reflux (reaction time shown in Table 1). The solution was cooled to 0 °C. Then *n*-BuLi (1.53 mL, 2.0 mmol, 1.3 M in hexanes) was added dropwise, and stirring continued for 30 min. After this time, the mixture reached the room temperature and a solution of iodine [1.01 g, 4.0 mmol in THF (5.0 mL)] was transferred to the flask via syringe. The products were extracted with ethyl acetate (100 mL); the organic phase was washed with brine (3×50 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel (230–400 mesh) using hexane as mobile phase in all cases to give the corresponding (***E***)-iodo(thio)ketene acetals as yellow oil.

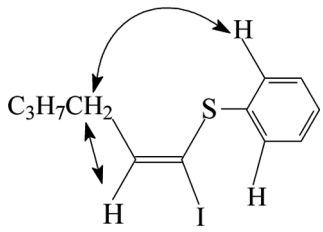
Data

(***E***)-1-Iodo-1-phenylthio-1-pentene **6a**

Yield: 80% (0.24 g). ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 0.9 (t, $J = 7.5$ Hz, 3H), 1.4 (sext, $J = 7.5$ Hz, 2H), 2.3 (q, $J = 7.5$ Hz, 2H), 6.9 (t, $J = 7.5$ Hz,

1H), 7.1–7.5 (m, 5H); ^{13}C NMR (75 MHz) (δ in $CDCl_3$) 13.7, 21.3, 39.7, 86.7, 127.3, 129.1, 129.9, 129.9, 132.4, 135.5, 152.9. MS m/z (%) 304 (19.83), 177 (100.0), 149 (10.13), 121 (49.98), 71 (52.10), 67 (45.77). Anal. calc. for $C_{11}H_{13}SI$: C, 43.43; H, 4.23. Found: C, 43.00; H, 4.32.

(***E***)-1-Iodo-1-phenylthio-1-hexene **6b**



6b

Observed NOESY correlations

H_{vinyl}/CH_2(allylic)

CH_2(allylic)/CH(aromatic)

Yield: 79% (0.25 g). ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 0.9 (t, $J = 7.5$ Hz, 3H), 1.3–1.5 (m, 4H), 2.2 (q, $J = 7.5$ Hz, 2H), 6.9 (t, $J = 7.5$ Hz, 1H), 7.1–7.6 (m, 5H); ^{13}C NMR (75 MHz) 13.9, 22.3, 30.0, 37.5, 86.4, 127.1, 127.2, 127.4, 129.0, 129.8, 135.5, 151.9. MS m/z (%) 318 (9.54), 191 (25.33), 149 (46.83), 116 (28.13), 81 (100.0), 51 (2.52). Anal. calc. for $C_{12}H_{15}SI$: C, 45.26; H 4.75. Found: C, 45.63; H, 4.54.

(***E***)-1-Iodo-1-phenylthio-2-phenyl Ethene **6c**

Yield: 75% (0.25 g). ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 7.1–7.2 (m, 11H); ^{13}C NMR (75 MHz) 86.5, 127.1, 127.2, 127.4, 127.7, 129.0, 129.3, 129.8, 129.9, 135.5, 135.8, 152.6. MS m/z (%) 338 (23.76), 211 (30.44), 134 (100.0), 102 (56.7), 77 (12.3). Anal. calc. for $C_{14}H_{11}SI$: C, 49.76; H, 3.25. Found: C, 49.52; H, 3.12.

(***E***)-1-Iodo-1-phenylthio-2-cyclohexenyl Ethene **6d**

Yield: 70% (0.24 g). ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 1.5–2.1 (m, 8H), 5.8 (m, 1H), 6.8 (s, 1H), 7.1–7.6 (m, 5H); ^{13}C NMR (75 MHz) (δ in $CDCl_3$) 21.6, 23.1, 23.4, 24.5, 87.4, 128.5, 128.7, 129.5, 131.4, 132.5, 135.1, 135.8, 138.5, 151.3. MS m/z (%) 342 (54.34), 215 (34.54), 106 (5.67), 71 (23.6). Anal. calc. for $C_{14}H_{15}SI$: C, 49.12; H, 4.34. Found: C, 48.87; H, 4.54.

(*E*)-1-Iodo-1-phenylthio-3-tetrahydropyranyl-1-propene **6e**

Yield: 65% (0.24 g). ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 1.65 (br, THP methylenes), 3.5 (d, $J = 7.5$ Hz, 2H), 6.9 (t, $J = 7.5$ Hz, 1H), 7.1–7.5 (m, 5H); ^{13}C NMR (75 MHz) (δ in $CDCl_3$) 10.6, 13.4, 21.8, 32.9, 58.6, 75.6, 87.7, 126.3, 126.7, 127.3, 128.9, 132.3, 139.6, 151.2. MS m/z (%) 376 (6.78), 249 (13.43), 172 (100.0), 140 (6.78), 77 (45.5). Anal. calc. for $C_{14}H_{17}SIO_2$: C, 44.61; H, 4.54. Found: C, 44.2; H, 4.34.

(*E*)-1-Iodo-1-phenylthio-3-methyl-1,3-butadiene **6f**

Yield: 60% (0.18 g). ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 0.9 (t, $J = 7.5$ Hz, 3H), 5.2 (q, $J = 1.0$ Hz, 1H), 5.3 (s, 1H), 6.8 (s, 1H), 7.2–7.4 (m, 5H); ^{13}C NMR (75 MHz) (δ in $CDCl_3$) 13.5, 86.9, 103.1, 126.5, 128.6, 132.4, 128.31, 138.3, 139.4, 140.4, 151.8. MS m/z (%) 302 (6.76), 175 (14.83), 98 (100.0), 83 (21.23), 77 (34.87). Anal. calc. for $C_{11}H_{11}SI$: C, 43.76; H, 3.65. Found: C, 44.00; H, 3.52.

General Procedure for (*E*)-Vinyl Sulfides

A solution of *n*-BuLi (1.53 mL, 2.0 mmol, 1.3 M in hexanes) was added dropwise to a flask containing a solution of DIBAL-H (2.0 mL, 2.0 mmol, 1.0 M in hexanes) in THF (10 mL) at 0 °C under N_2, and the mixture was stirred for 30 min. Then, a solution of thioacetylene (1.0 mmol) in THF (2.0 mL) was added, and the mixture was stirred under reflux (reaction time shown in Table 1). After this time, the mixture reached the room temperature, and water (5.0 mL) was transferred to the flask via syringe. It was stirred, and the product was extracted with ethyl acetate (100 mL). The organic phase was washed with brine (3×50 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure, and the crude product was purified by flash chromatography on silica gel (230–400 mesh) using hexane as mobile phase in all cases, giving the (*E*)-vinyl sulfides as yellow oil.

Data

(*E*)-1-Phenylthio-1-pentene **4a**

Yield: 80% (0.14 g) ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 0.9 (t, $J = 7.5$ Hz, 3H), 1.5 (m, 2H), 2.2 (dt, $J = 7.5$ Hz, 2H), 6.1 (dt, $J = 15.0$ Hz, $J = 7.5$ Hz, 1H), 6.5 (d, $J = 15.0$ Hz, 1H), 7.1–7.4 (m, 5H); ^{13}C NMR (20 MHz) (δ in $CDCl_3$)

12.4, 22.1, 31.3, 125.3, 126.5, 128.5, 129.3, 135.3, 135.9, 138.7, 138.5. Anal. calc. for $C_{11}H_{14}S$: C, 74.10; H, 7.81. Found: C, 73.61; H, 7.34.

(*E*)-1-Phenylthio-1-hexene **4b**

Yield: 79% (0.15 g). ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 1.0 (t, $J = 7.5$ Hz, 3H), 1.1–1.6 (m, 4H), 2.4 (dt, $J = 7.5$ Hz, 2H), 5.3 (dt, $J = 15.0$ Hz, $J = 7.5$ Hz, 1H), 6.4 (d, $J = 15.0$ Hz, 1H), 7.2 (m, 5H); ^{13}C NMR (20 MHz) (δ in $CDCl_3$) 12.4, 22.5, 29.1, 30.3, 125.3, 126.4, 128.7, 129.8, 135.2, 135.7, 138.6, 138.6. Anal. calc. for $C_{12}H_{16}S$: C, 75.11; H, 8.38. Found: C, 75.54; H, 8.98.

(*E*)-1-Phenylthio-2-phenyl Ethene **4c**

Yield: 75% (0.16 g). ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 6.4 (d, $J = 15.0$ Hz, 1H), 6.6 (d, $J = 15.0$ Hz, 1H), 7.5 (m, 10H); ^{13}C NMR (20 MHz) (δ in $CDCl_3$) 124.3, 124.5, 125.0, 125.5, 126.4, 126.8, 128.5, 128.5, 129.6, 130.4, 131.9, 132.5, 135.8, 139.3. Anal. calc. for $C_{14}H_{12}S$: C, 79.22; H, 5.65. Found: C, 78.98; H, 5.23.

(*E*)-1-Phenylthio-2-cyclohexenyl Ethene **4d**

Yield: 75% (0.16 g). ^{1}H NMR (80 MHz) (δ in $CDCl_3$) 1.5–2.1 (m, 8H), 5.7 (m, 1H), 6.2 (d, $J = 14.5$ Hz, 1H), 6.3 (d, $J = 14.5$ Hz, 1H), 7.3 (m, 5H); ^{13}C NMR (20 MHz) (δ in $CDCl_3$) 21.5, 22.3, 23.1, 24.5, 129.1, 128.7, 129.3, 130.4, 131.3, 135.1, 135.5, 138.5, 139.4, 142.2. Anal. calc. for $C_{14}H_{16}S$: C, 77.72; H, 7.42. Found: C, 77.32; H, 7.71.

(**E**)-1-Phenylthio-3-tetrahydropyranyl-1-propene **4e**

Yield: 65% (0.16 g). ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 1.62 (br, THP methylenes), 3.5 (d, $J = 7.5$ Hz, 2H), 6.2 (dt, $J = 14.3$ Hz, $J = 7.5$ Hz, 1H), 6.5 (d, $J = 14.3$ Hz, 1H), 7.3 (m, 5H); ^{13}C NMR (75 MHz) (δ in $CDCl_3$) 10.6, 13.4, 21.8, 30.9, 58.6, 74.6, 126.3, 126.7, 127.3, 128.9, 132.3, 134.7, 139.6, 142.2. Anal. calc. for $C_{14}H_{18}SO_2$: C, 67.20; H, 7.20. Found: C, 67.51; H, 7.05.

(*E*)-1-Phenylthio-3-methyl-1,3-butadiene **4f**

Yield 67% (0.11 g). ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 0.9 (t, $J = 7.5$ Hz, 3H), 5.2 (q, $J = 1.0$ Hz, 1H), 5.3 (s, 1H), 6.6 (d, $J = 15.0$ Hz, 1H), 6.89 (d, $J = 15.0$ Hz, 1H), 7.3 (m, 5H); ^{13}C NMR (75 MHz) (δ in $CDCl_3$) 13.5,

103.2, 112.31, 126.5, 127.6, 129.3, 131.2, 128.31, 138.3, 139.4, 146.1. Anal. calc. for $C_{11}H_{12}S$: C, 75.00; H, 6.91. Found: C, 75.32; H, 6.91.

General Procedure for (Z)-Iodo(ketene)acetals

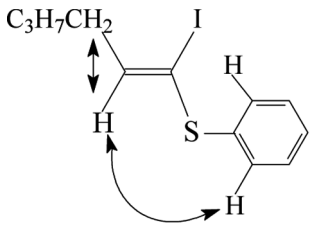
A solution of *n*-BuLi (1.53 mL, 2.0 mmol, 1.3 M in hexanes) was added dropwise to a flask containing a solution of DIBAL-H (2.0 mL, 2.0 mmol, 1.0 M in hexanes) in THF (10 mL) at 0 °C under N_2 and the mixture was stirred for 30 min. Then, a solution of thioacetylene (1.0 mmol) in THF (2.0 mL) was added, and the mixture was stirred under reflux (reaction time shown in Table 1). After this time, the mixture reached room temperature, and a solution of iodine [1.01 g, 4.0 mmol in THF (5.0 mL)] was transferred to the flask via syringe. It was stirred, and the product was extracted with ethyl acetate (100 mL). The organic phase was washed with brine (3×50 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure, and the crude product was purified by chromatography flash on silica gel (230–400 mesh) using hexane as mobile phase in all cases, giving the (**Z**)-iodo(thio)ketene acetals as yellow oil.

Data

(**Z**)-1-Phenylthio-1-iodo-1-pentene **7a**

Yield: 78% (0.23 g). ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 0.9 (t, $J = 7.5$ Hz, 3H), 1.5 (sext, $J = 7.5$ Hz, 2H), 2.2 (q, $J = 7.5$ Hz, 2H), 6.3 (t, $J = 7.5$ Hz, 1H), 7.2–7.4 (m, 5H); ^{13}C NMR (75 MHz) (δ in $CDCl_3$) 13.7, 21.3, 39.7, 91.2, 127.3, 127.4, 129.2, 129.8, 129.9, 135.5, 148.4. MS *m/z* (%) 304 (19.37), 177 (100.0), 143 (24.08), 135 (30.34), 71 (27.17), 67 (31.26). Anal. calc. for $C_{11}H_{13}SI$: C, 43.43; H 4.23. Found: C, 43.72; H, 4.12.

(**Z**)-1-Iodo-1-phenylthio-1-hexene **7b**



7b

Observed NOESY correlations

H_{vinyl}/CH(aromatic)

H_{vinyl}/CH_2(allylic)

Yield: 81% (0.26 g). ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 0.9 (t, $J = 7.5$ Hz, 3H), 1.3–1.5 (m, 4H), 2.2 (q, $J = 7.5$ Hz, 2H), 6.3 (t, $J = 7.5$ Hz, 1H), 7.2–7.4 (m, 5H); ^{13}C NMR (75 MHz) (δ in $CDCl_3$) 13.9, 22.2, 30.0, 37.5, 91.0, 127.1, 127.2, 127.4, 129.0, 129.8, 135.5, 148.6. MS m/z (%) 318 (7.62), 250 (12.6), 218 (31.83), 191 (13.27), 149 (20.17), 110 (100.0), 81 (25.30), 32 (14.09). Anal. calc. for $C_{12}H_{15}SI$: C, 45.26; H 4.75. Found C, 44.91; H, 4.62.

(**Z**)-1-Iodo-1-phenylthio-2-phenyl Ethene **7c**

Yield: 70% (0.23 g). ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 6.9 (s, 1H), 7.1–7.2 (m, 10H); ^{13}C NMR (75 MHz) (δ in $CDCl_3$) 90.1, 127.2, 127.4, 127.4, 127.9, 129.3, 129.5, 129.8, 129.9, 135.7, 135.8, 148.9. MS m/z (%) 338 (4.62), 211 (45.76), 134 (100.0), 102 (3.45), 77 (5.76). Anal. calc. for $C_{14}H_{11}SI$: C, 49.76; H, 3.25. Found: C, 49.52; H, 3.55.

(**Z**)-1-Iodo-1-phenylthio-2-cyclohexenyl Ethene **7d**

Yield: 69% (0.23 g). ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 1.5–2.1 (m, 8H), 5.8 (m, 1H), 6.2 (s, 1H), 7.1–7.6 (m, 5H); ^{13}C NMR (75 MHz) (δ in $CDCl_3$) 21.9, 23.3, 23.6, 24.5, 91.4, 128.7, 128.9, 129.5, 131.4, 132.5, 135.1, 138.5, 139.4, 148.3. MS m/z (%) 342 (34.56), 215 (23.45), 138 (100.0), 106 (6.54). Anal. calc. for $C_{14}H_{15}SI$: C, 49.12; H, 4.34. Found: C, 49.32; H, 4.4.

(**Z**)-1-Iodo-1-phenylthio-3-tetrahydropyranyl 1-Propene **7e**

Yield: 60% (0.22 g). ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 1.62 (br, THP methylenes), 3.3 (d, $J = 7.5$ Hz, 2H), 6.2 (t, $J = 7.5$ Hz, 1H), 7.2–7.6 (m, 5H); ^{13}C NMR (75 MHz) (δ in $CDCl_3$) 10.7, 13.5, 21.8, 32.9, 58.6, 75.6, 92.1, 126.3, 126.7, 127.5, 129.2, 132.3, 139.6, 148.1. MS m/z (%) 376 (5.98), 249 (7.78), 172 (100.0), 140 (3.45), 52 (32.5). Anal. calc. for $C_{14}H_{17}SIO_2$: C, 44.61; H, 4.54. Found: C, 44.8; H, 4.12.

(**Z**)-1-Iodo-1-phenylthio-3-methyl-1,3-butadiene **7f**

Yield: 65% (0.19 g). ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 0.9 (t, $J = 7.5$ Hz, 3H), 5.2 (q, $J = 1.0$ Hz, 1H), 5.3 (s, 1H), 6.2 (s, 1H), 7.2–7.4 (m, 5H); ^{13}C NMR (75 MHz) (δ in $CDCl_3$) 13.5, 91.9, 104.1, 126.8, 128.8, 132.4, 128.3, 138.3, 139.4, 140.4, 149.4. MS m/z (%) 302 (4.56), 175 (100.0), 98 (7.65), 77 (7.65), 66 (23.76) Anal. calc. for $C_{11}H_{11}SI$: C, 43.76; H, 3.65. Found: C, 43.32; H, 3.32.

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